

Sulfur and Moisture Effects on Alumina Scale and TBC Spallation

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Presented at GE Aviation, Evendale, OH May 9, 2007

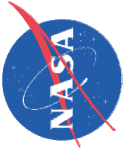
It has been well established that a few ppmw sulfur impurity may segregate to the interface of thermally grown alumina scales and the underlying substrate, resulting in bond degradation and premature spallation. This has been shown for NiAl and NiCrAl-based alloys, bare single crystal superalloys, or coated superalloys. The role of reactive elements (especially Y) has been to getter the sulfur in the bulk and preclude interfacial segregation. Pt additions are also very beneficial, however a similar thermodynamic explanation does not apply.

The purpose of the present discussion is to highlight some observations of these effects on Rene'142, Rene'N5, PWA1480, and PWA1484. For PWA1480, we have mapped cyclic oxidation and spallation in terms of potential sulfur interfacial layers and found that a cumulative amount of about one monolayer is sufficient to degrade long term adhesion. Depending on substrate thickness, optimum performance occurs if sulfur is reduced below about 0.2-0.5 ppmw. This is accomplished in the laboratory by hydrogen annealing or commercially by melt-fluxing.

Excellent 1150°C cyclic oxidation is thus demonstrated for desulfurized Rene'142, Rene'N5, and PWA1484. Alternatively, a series of N5 alloys provided by GE-AE have shown that as little as 15 ppmw of Y dopant was effective in providing remarkable scale adhesion. In support of a Y-S gettering mechanism, hydrogen annealing was *unable* to desulfurize these alloys from their initial level of 5 ppmw S. This impurity and critical doping level corresponds closely to YS or Y₂S₃ stoichiometry.

In many cases, Y-doped alloys or alloys with marginal sulfur levels exhibit an oxidative sensitivity to the ambient humidity called **Moisture-Induced Delayed Spallation (MIDS)**. After substantial scale growth, coupled with damage from repeated cycling, cold samples may spall after a period of time, breathing on them, or immersing them in water. While stress corrosion arguments may apply, we propose that the underlying cause is related to a hydrogen embrittlement reaction: $\text{Al}_{\text{alloy}} + 3 \text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3\text{H}^+ + 3\text{e}^-$. This mechanism is derived from an analogous moisture-induced hydrogen embrittlement mechanism originally shown for Ni₃Al and FeAl intermetallics. Consequently, a cathodic hydrogen charging technique was used to demonstrate that electrolytic de-scaling occurs for these otherwise adherent alumina scales formed on Y-doped Rene'N5, in support of hydrogen effects.

Finally, some TBC observations are discussed in light of all of the above. Plasma sprayed 8YSZ coatings, produced on PWA1484 without a bond coat, were found to survive more than 1000 1-hr cycles at 1100°C when desulfurized to below 0.1 ppmw. At higher sulfur (1.2 ppmw) levels, moisture sensitivity and delayed TBC failure, referred to as '**Desk Top Spallation**,' occurred at just 200 hr. Despite a large degree of scatter, a factor of 5 in life improvement is indicated for desulfurized samples in cyclic furnace tests, confirming the beneficial effect of low sulfur alloys on model TBC systems. (DTS and moisture effects are also observed on commercially applied PVD 7YSZ coatings on Rene'N5+Y with Pt-aluminide bond coats). These types of catastrophic failure were subverted on the model system by segmenting the substrate into a network of 0.010" high ribs, spaced ¼ in. apart, prior to plasma spraying. No failures occurred after 1000 cycles at 1150°C or after 2000 cycles at 1100°C, even after water immersion. The benefit is described in terms of elasticity models and a critical buckling stress.



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Outline of Review

- Overview of compositional effects
- Critical sulfur content and Y/S ratio
- Moisture-induced delayed spallation;
- Desk Top Spallation
- Cyclic models (COSP for Windows)



Compositions and Prevalent Scale Components (weight %)

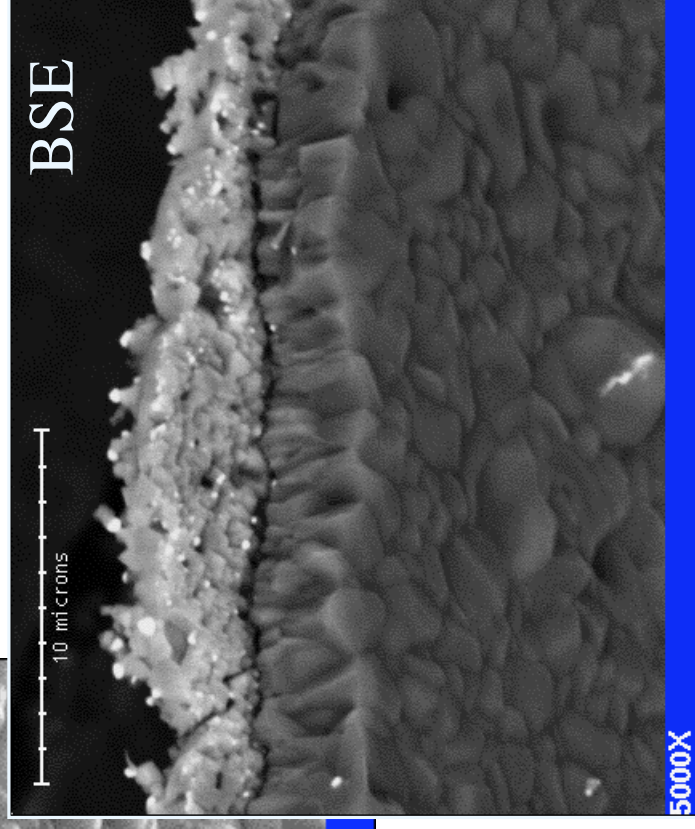
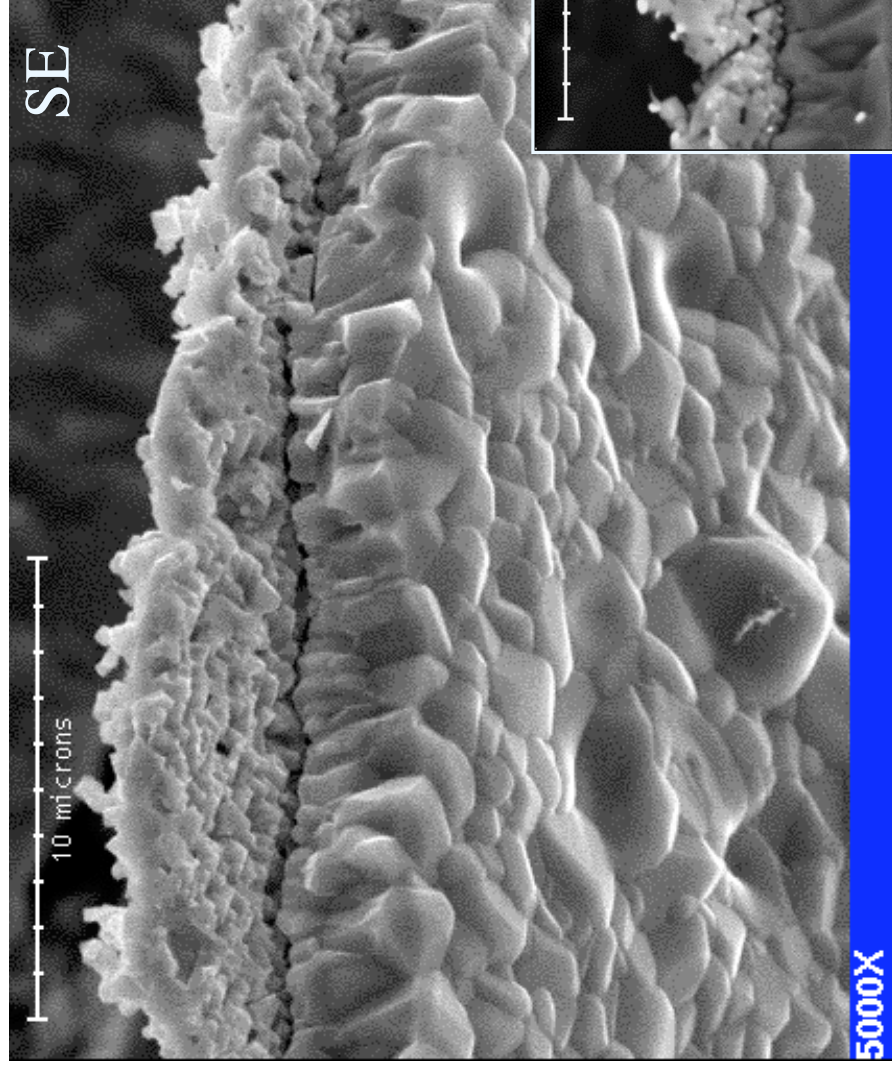
alloy	Co	Al	Cr	Ta	W	Mo	Re	Ti	Hf	S	Y
										ppmw	ppmw
PWA 1480	5	5.0	10	12	4	0	0	1.5	0.0	6.7	0.0
PWA 1484	10	5.6	5	9	6	2	3	0.0	0.1	1.2	0.0
(René 142)	13	6.2	6	6	6	13	3.5	0.0	2.0	6.1	0.0
René N5	8	6.2	7	7	5	2	3	0.0	0.2	3-6	0-100

Al_2O_3 , $\text{Ni}(\text{Al,Cr})_2\text{O}_4$, CrTaO_4 , NiTa_2O_6 , HfO_2 , Cr_2O_3 , NiO , TiO_2
(protective, neutral, detrimental)



Oxidation Issues for Ni-base Superalloys

- Al_2O_3 protective scales; external vs internal oxidation
- NiAl_2O_4 , NiTa_2O_6 , CrTaO_4 relatively innocuous
- Layered: a) NiAl_2O_4 , NiTa_2O_6 outer transients
b) Al_2O_3 inner layer
- Cr_2O_3 (?), NiCr_2O_4 , NiO , TiO_2 , HfO_2 non-protective scale
- NiMoO_4 , NiWO_4 , CrNbO_4 , V_2O_5 , etc. also detrimental
- Co generally acts in concert with Ni
- S (adhesion) control: a) Y (Hf, Zr?) and gettering
b) or desulfurization



Transient Scale and Alumina
High S 1484, 1200°C, 25 h Air/75 h Ar

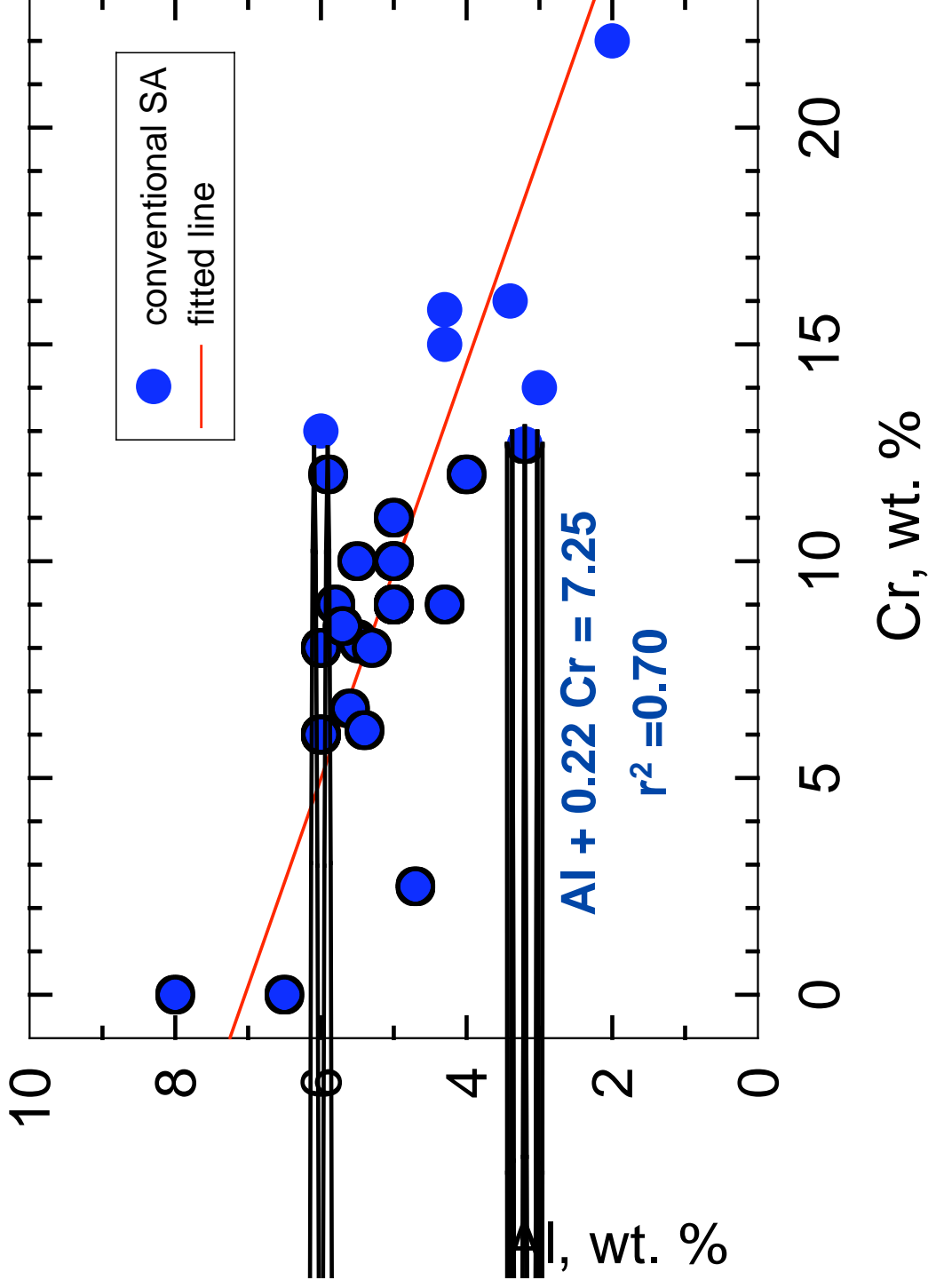


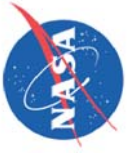
Ranking Diagram of 25 Ni Superalloys

	Alloy	$\Delta W/A$	Al	Cr	Ti	Ta	Nb	Mo	W	ratio	1/5Cr+Al
1	TAZ-8A	0.56	6.0	6.0	0	8	2.5	4	4	2.31	7.20
2	TRW-R	-0.96	5.3	8.0	0.8	6	0.3	3	4	1.35	6.90
3	B-1900	-1.40	6.0	8.0	1	4.3	0.1	6	0.1	1.41	7.60
4	NASA-TRW-VIA	-1.48	5.4	6.1	1	9	0.5	2	5.8	1.81	6.62
5	B-1900 + Hf	-1.68	6.0	8.0	1	4.3	0.1	6	0.1	1.41	7.60
6	MAR-M-247	-4.22	5.5	8.2	1	3	0	0.6	10	1.23	7.14
7	IN-713 LC	-6.20	5.9	12.0	0.6	0	2	4.5	0	0.90	8.30
8	PW-1480 SC	-7.44	5.0	10.0	1.5	12	0	0	4	1.12	7.00
9	TRW-1800	-8.65	6.0	13.0	0.6	0	1.5	0	9	0.85	8.60
10	Rene 125	-21.22	5.0	9.0	2.5	3.8	0	2	7	0.92	6.80
11	MAR-M-246	-24.44	5.0	11.0	1.5	2	0	0	0	0.81	7.20
12	Rene 120	-38.57	4.3	9.0	4	3.8	0	2	7	0.70	6.10
13	NX-188	-48.76	8.0	0.0	0	0	0	18	0		8.00
14	MAR-M-200	-53.59	5.0	9.0	2	0	1	0	12.5	0.86	6.80
15	U-700 Cast	-55.21	4.3	15.0	3.5	0	0	4.5	0	0.44	7.30
16	MAR-M-421	-74.11	4.3	15.8	1.8	0	2	2	3.8	0.47	7.46
17	MAR-M-200+Hf	-89.80	5.0	9.0	2	0	1	0	11.5	0.86	6.80
18	IN-792	-166.26	3.2	12.7	4.2	3.9	0	2	3.9	0.42	5.74
19	IN-100	-180.33	5.5	10.0	5.5	0	0	3	0	0.66	7.50
20	WAZ-20	-198.05	6.5	0.0	0	0	0	0	18.5		6.50
21	TAZ-8	-213.97	6.0	6.0	0	8	0	4	4	2.31	7.20
22	IN-939	-227.60	2.0	22.0	3.6	1.5	1	0	2	0.17	6.40
23	IN-738	-232.45	3.4	16.0	3.4	1.75	0.9	1.75	2.6	0.36	6.60
24	MAR-M-211	-269.76	5.0	9.0	2	0	2.7	2.5	5	0.86	6.80
25	Rene 80	-330.35	3.0	14.0	5	0	0	4	0	0.30	5.80
	1100°C, 200 hr	mg/cm ²								avg=	7.04
										stdev=	0.69



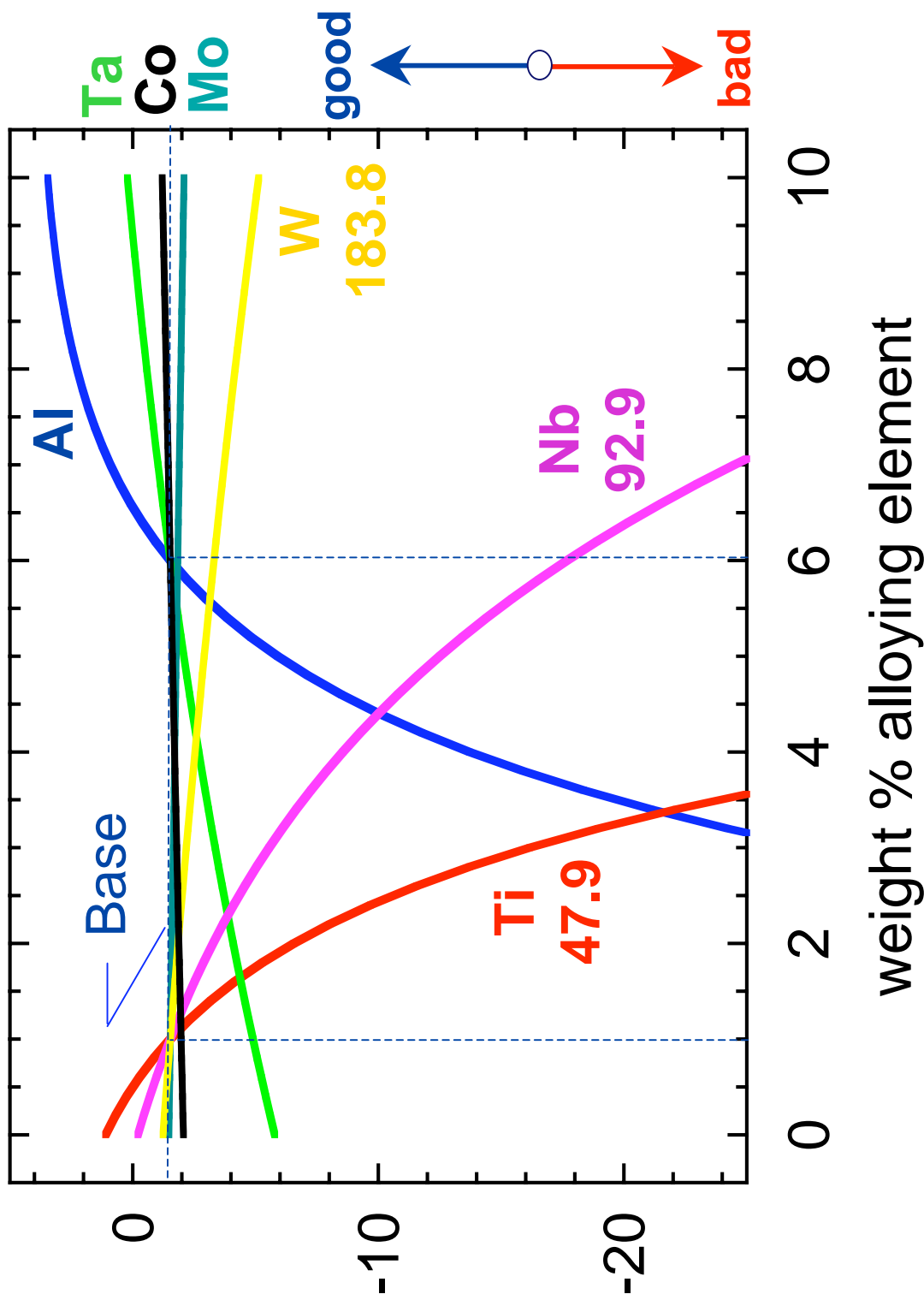
Inverse Correlation of Aluminum and Chromium in 25 Superalloys





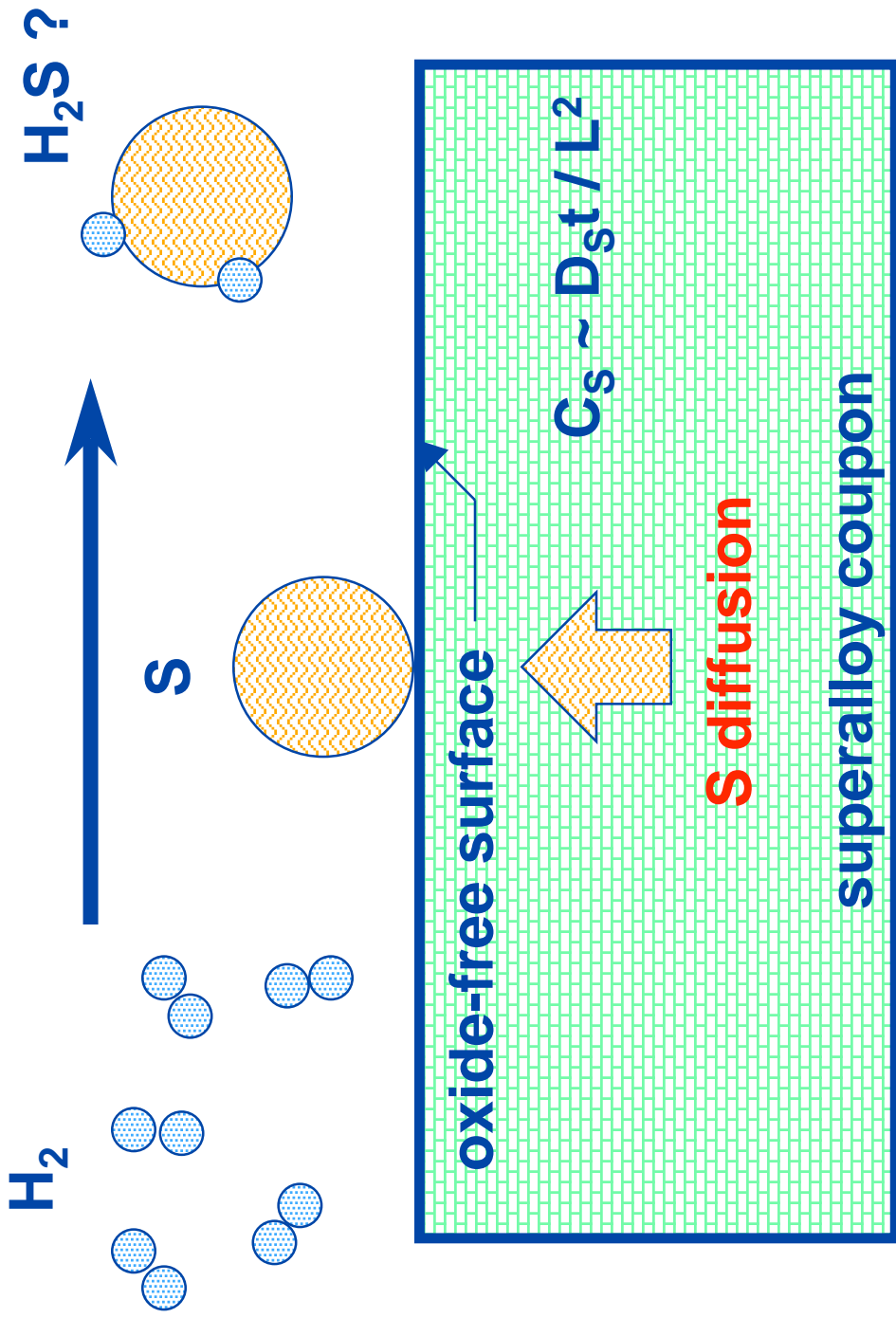
Predicted Cyclic Oxidation Weight Change

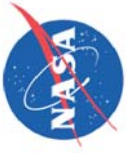
Ni-(6Co-6Al-6Cr-6Ta)-(1Ti-1Nb-1Mo-1W)-(0.2Hf-0.1C)



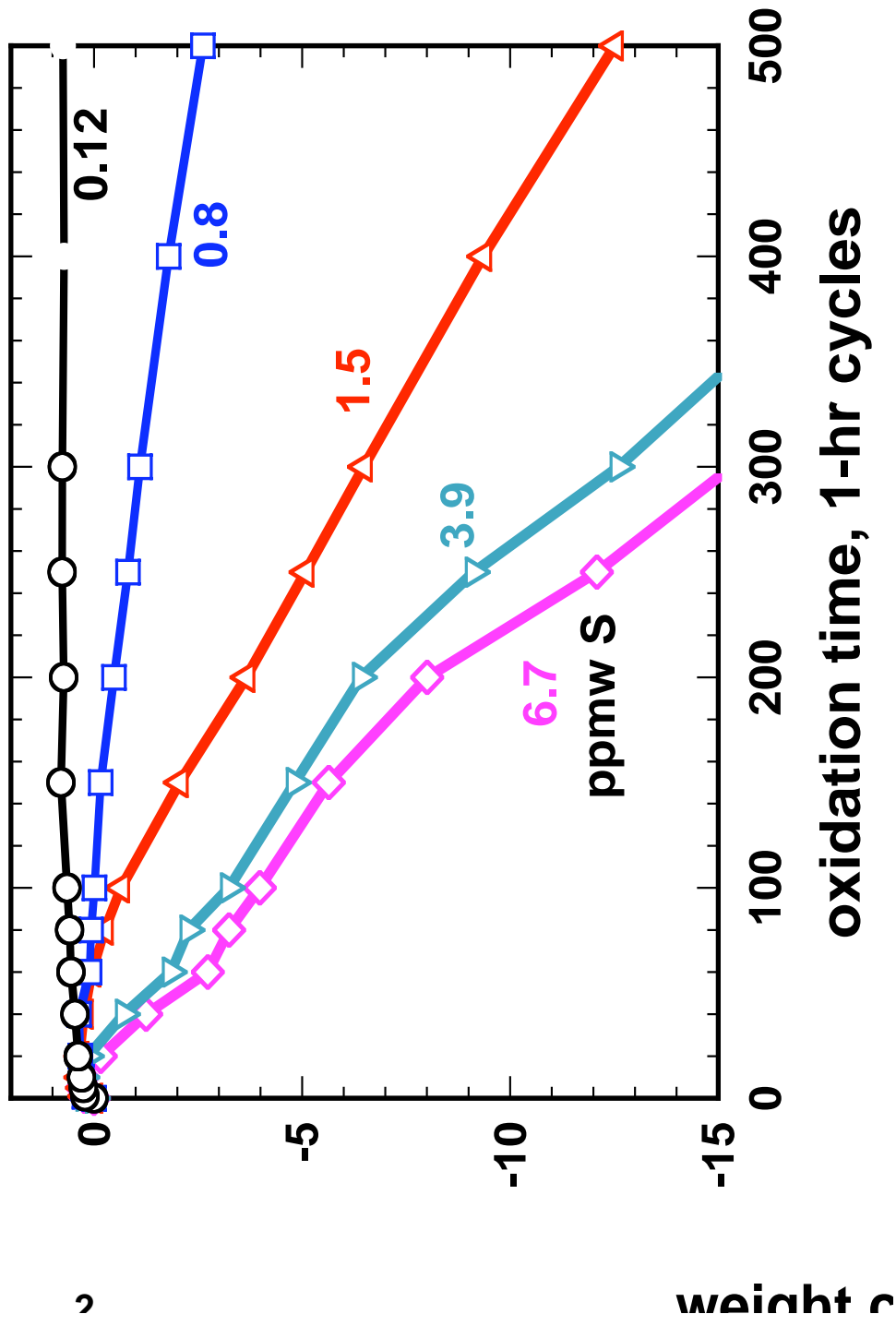


Diffusion Controlled Desulfurization





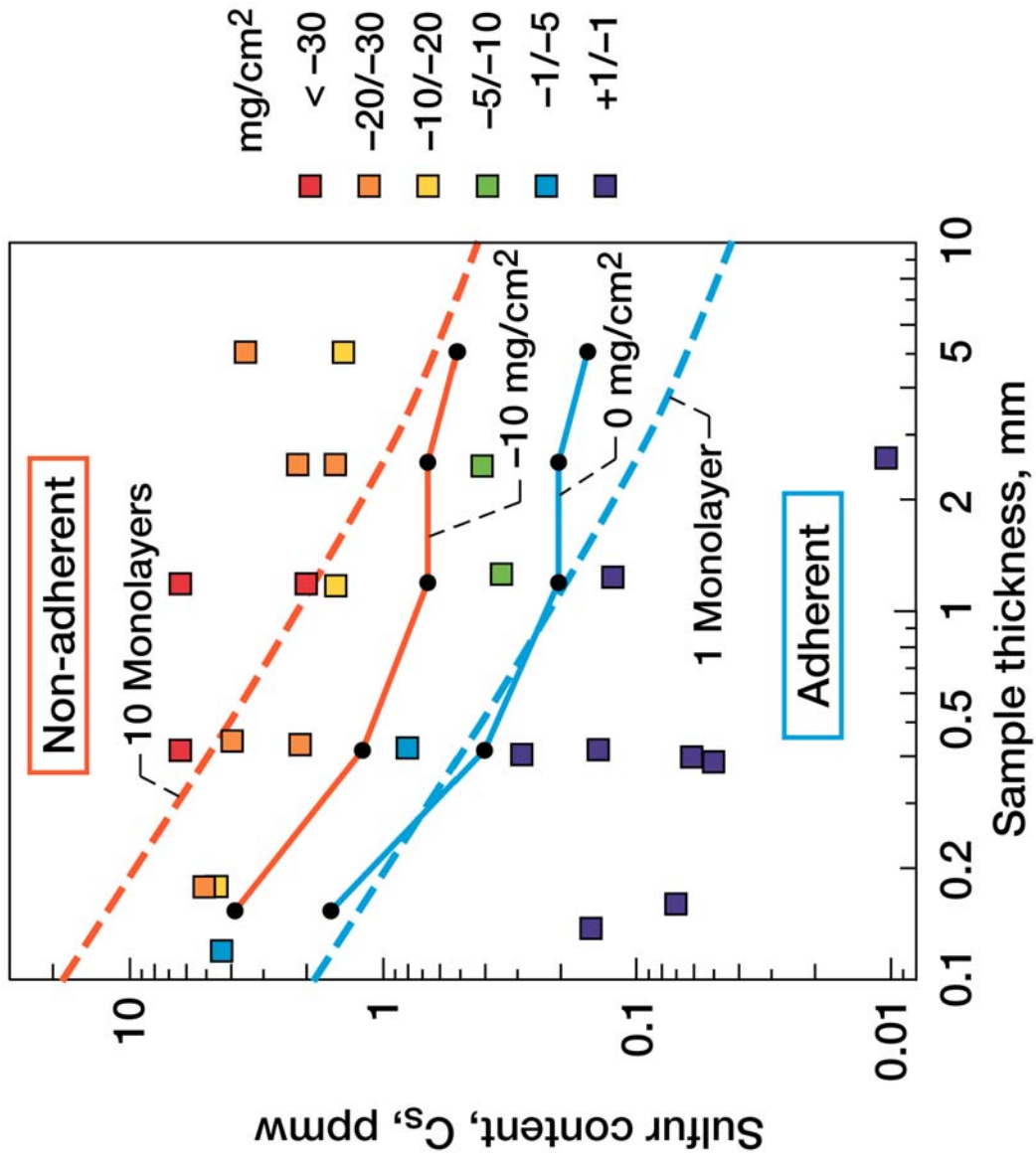
Effect of Sulfur Content on the 1100°C Cyclic Oxidation of PWA 1480

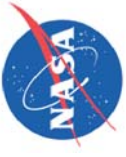




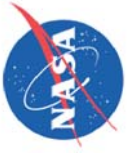
Oxide Adherence Map for Desulfurized PWA1480

1100 C, 1-hr Cycles, 500 Hours

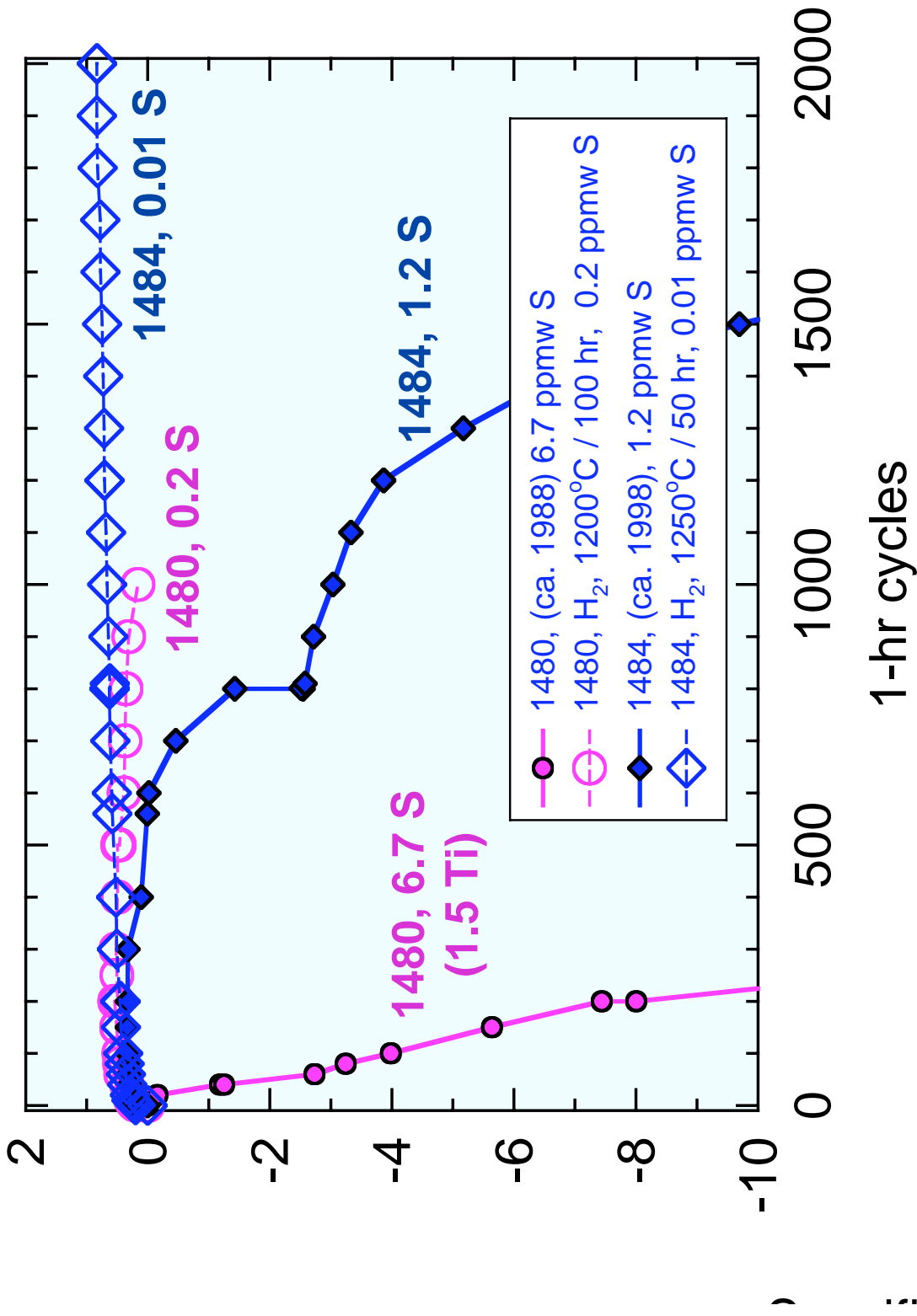


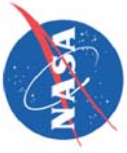


- **PWA 1480**
 - Distinct *critical sulfur content* and thickness effect
 - \approx ***0.2 ppmw S*** @ 1 mm (40 mils)
 - \approx ***1 monolayer*** total segregation (cf. 0.5 at saturation)

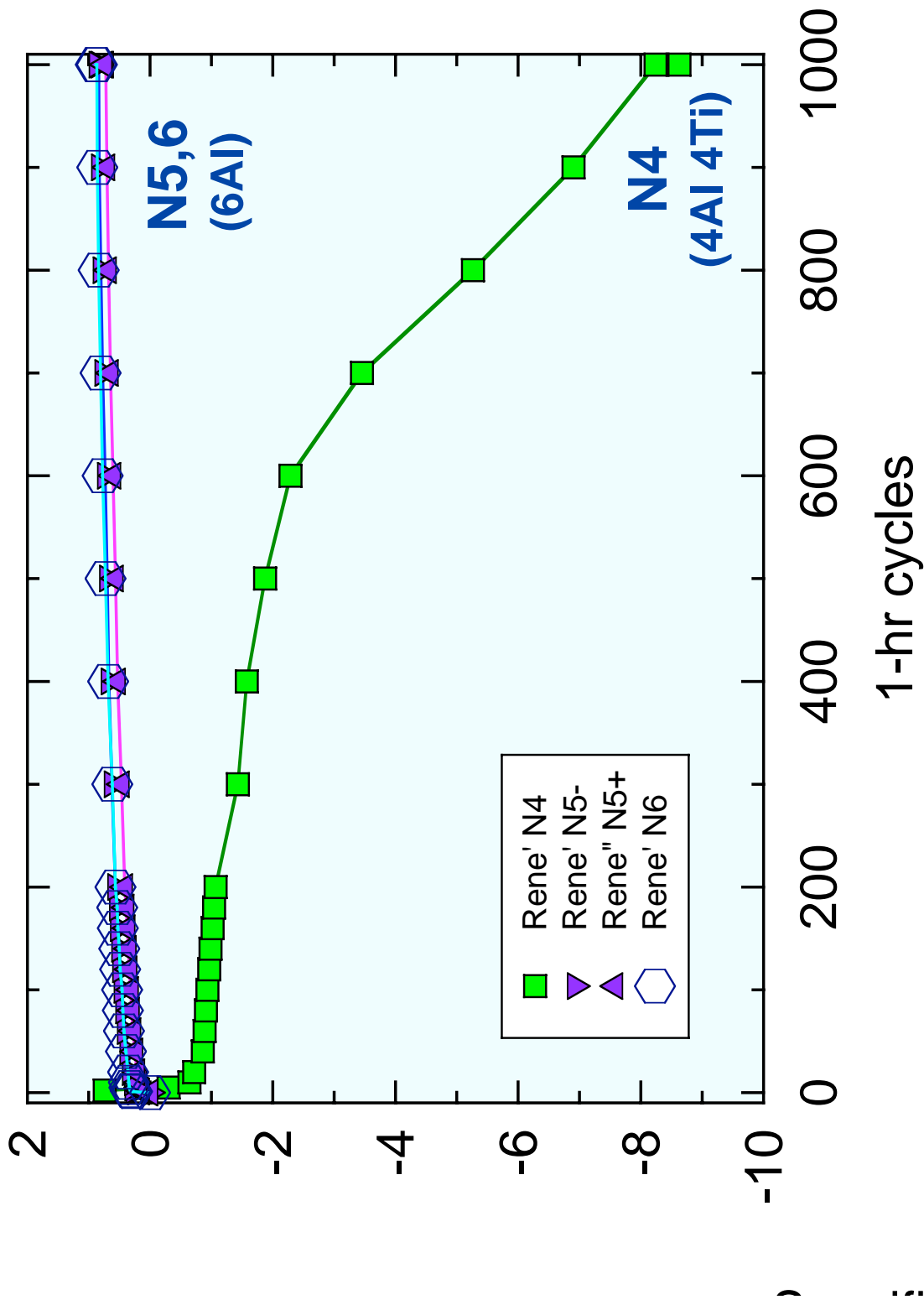


Improved 1100°C Cyclic Oxidation PWA 1480 to 1484





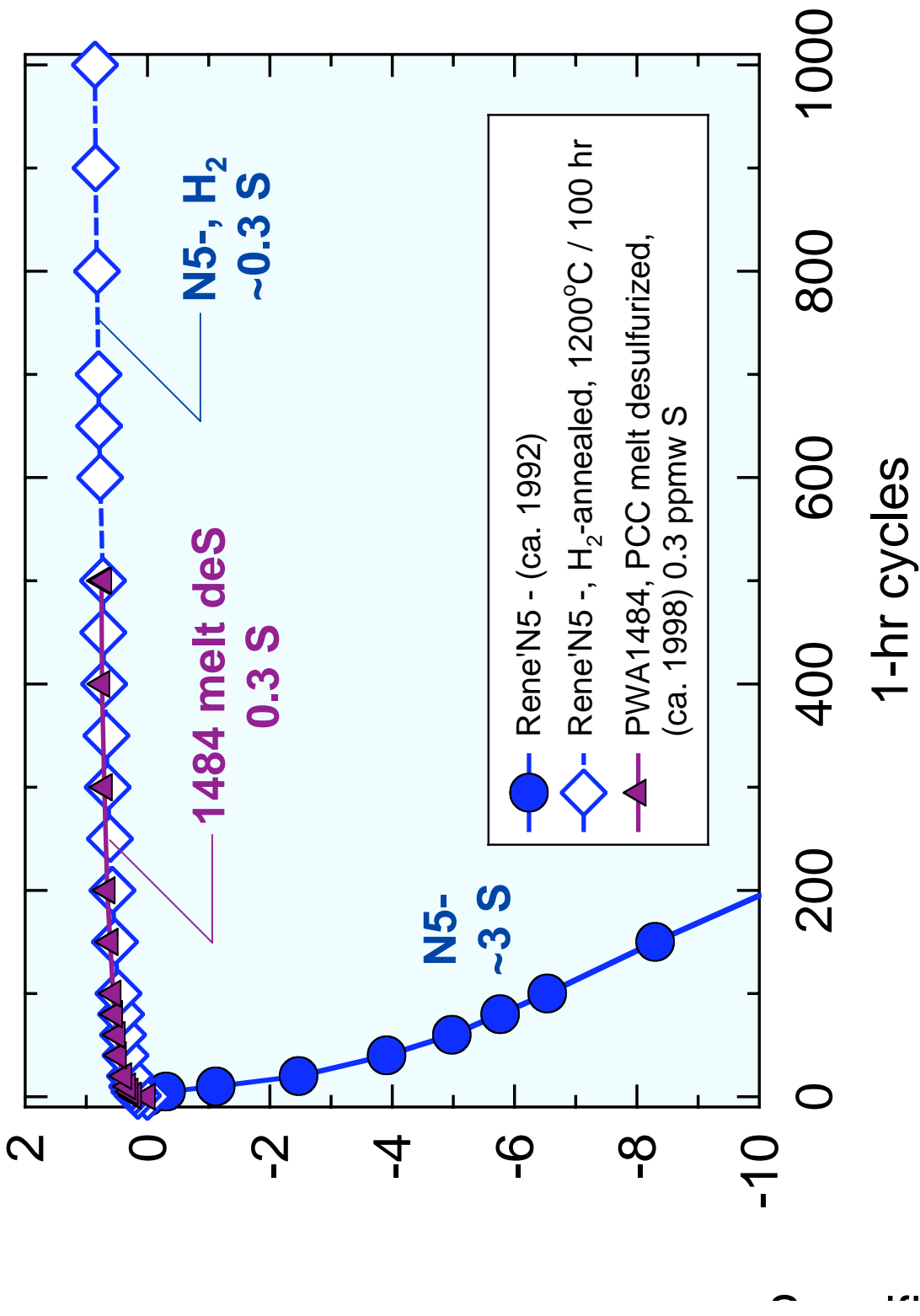
Improved 1100°C Cyclic Oxidation Rene'N4 to N5±Y, N6

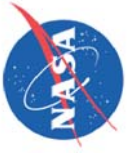




Exceptional 1150°C Cyclic Oxidation:

PWA 1484 and Rene'N5

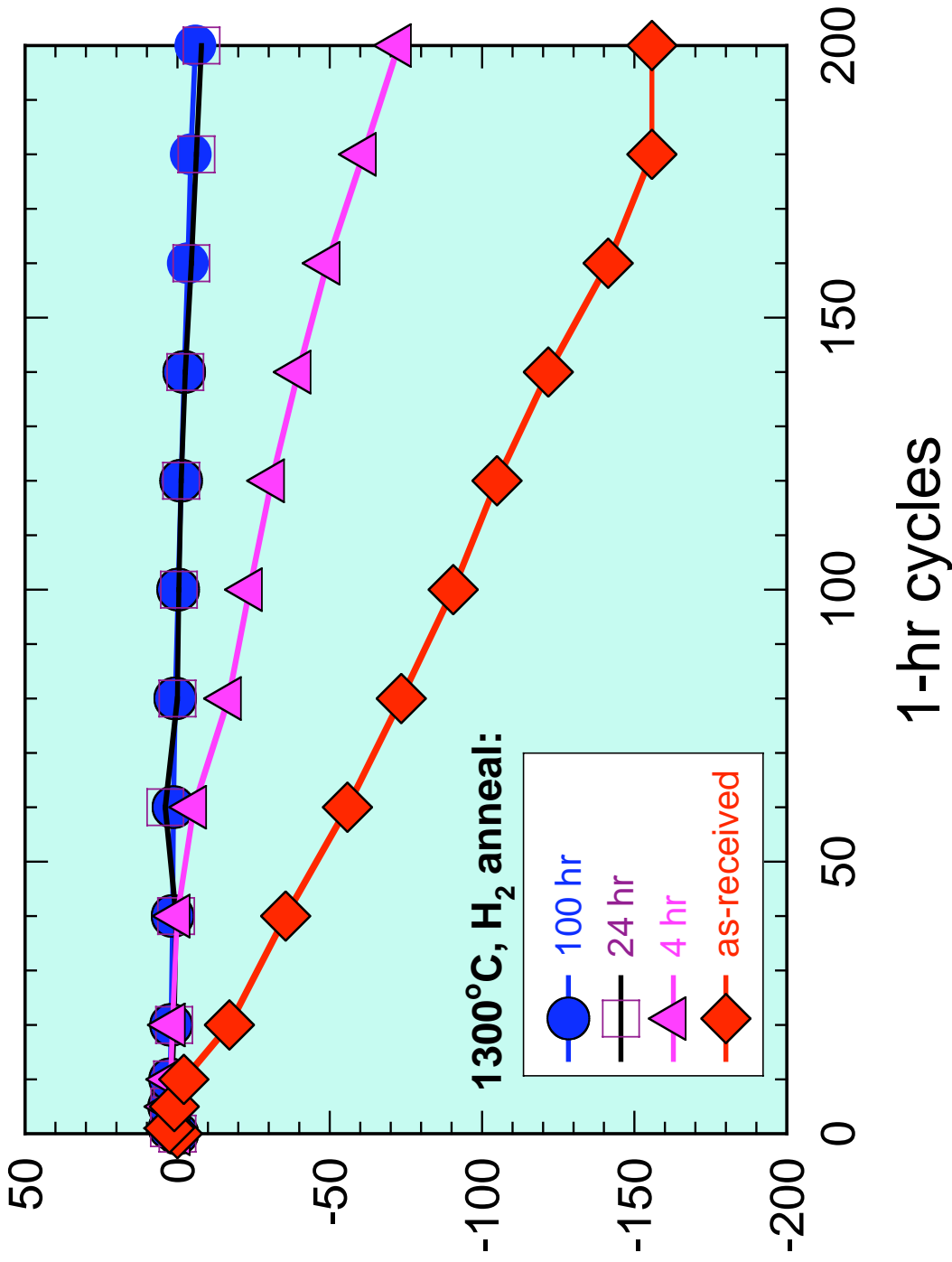




1100°C Cyclic Oxidation for EPM Alloy 39:

5.5Al 8.3Ta 20Co 2Mo

2.3Cr 4.5Ru 5.7Re 5.6W 0.4Ti

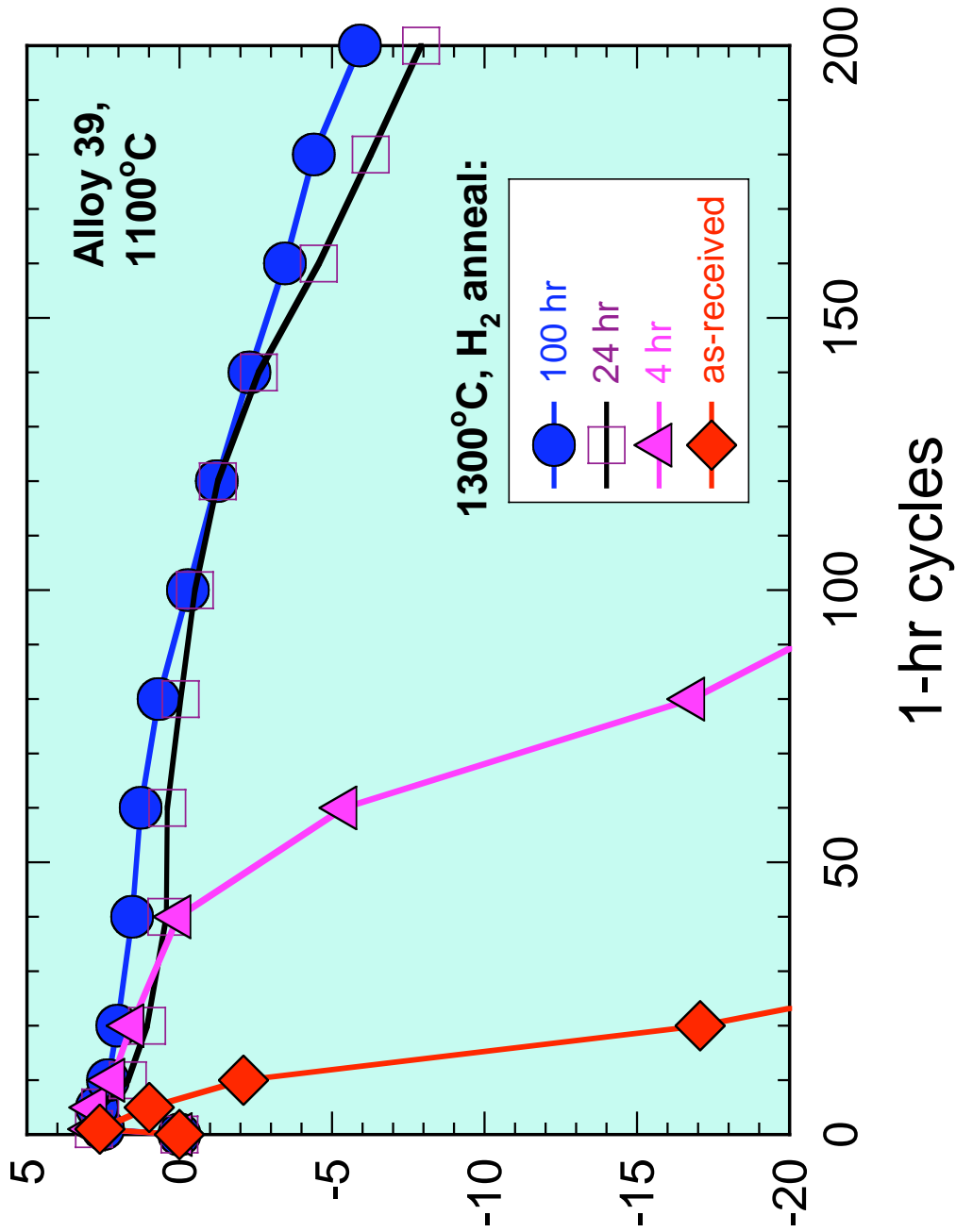


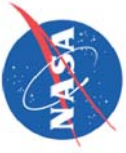


1100°C Cyclic Oxidation for EPM Alloy 39:

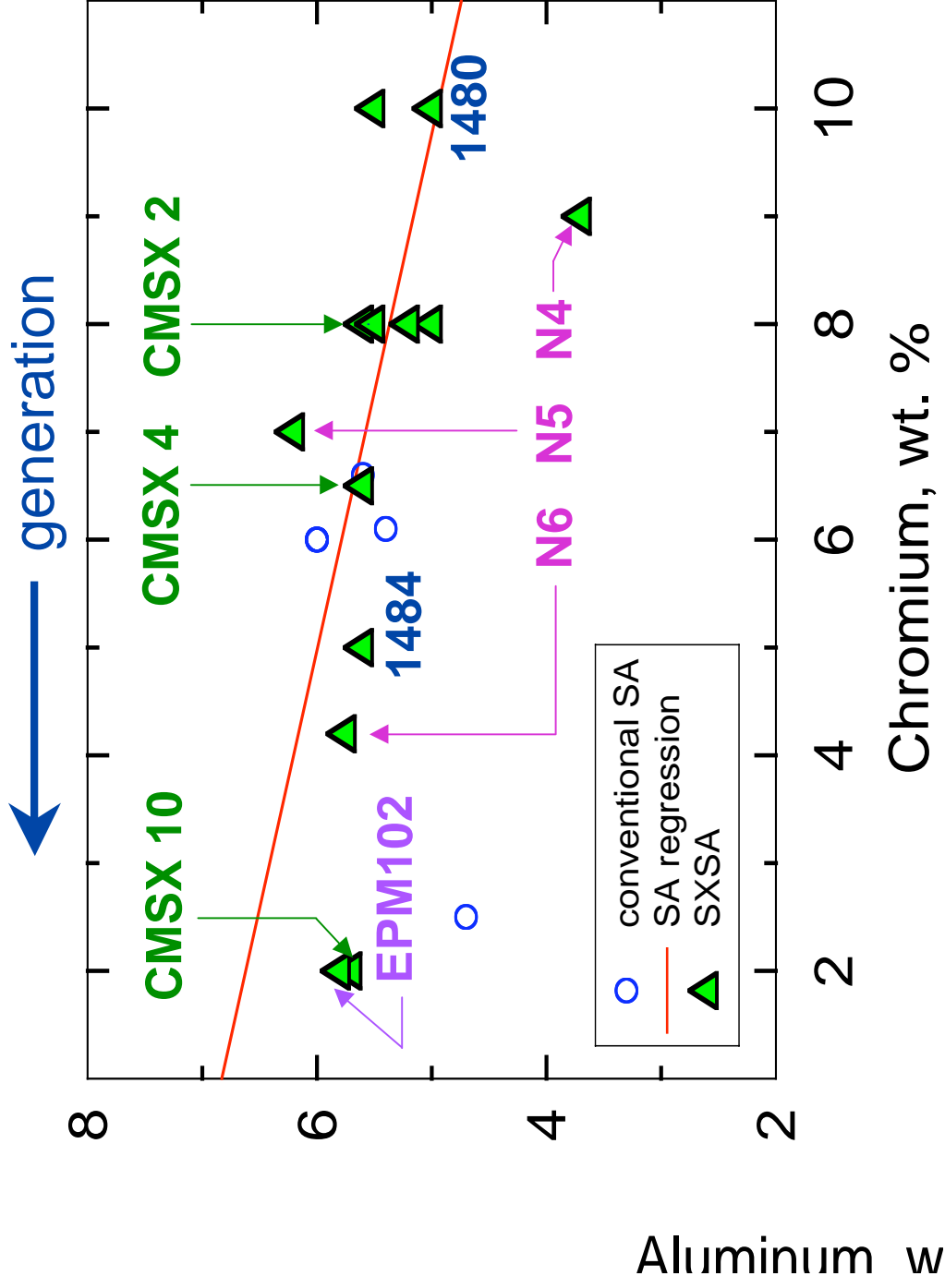
5.5Al 8.3Ta 20Co 2Mo

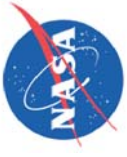
2.3Cr 4.5Ru 5.7Re 5.6W 0.4Ti





Reduced Chromium for Single Crystal Superalloys

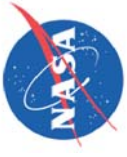




Room Temperature, Moisture-Induced Delayed Spallation (MIDS)

(NASA GRC Anecdotes)

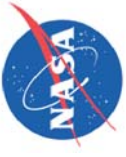
- 1978 NiAl: spalling over beaker of H₂O
- 1986 NiCrAl: sulfur purging (scale 'washed' off)
- 1989 PWA 1480: H₂-annealing (breath test)
- 1994 Rene'142, N5: H₂-annealing (immersion test)
- 1998 PWA 1484: melt, H₂-annealing (immersion)
- 2002 René N5: (immersion acoustic emission)



Moisture-Induced Spallation of Al_2O_3 Scales

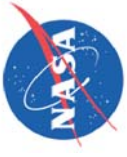
Additional Key Observations

- 1993, FeCrAl-Ce (Sigler, **GM**): more spallation in humid air, N_2 , Ar
- 1995, René N6 (Smith, Frazier, Pregger, **NAWC**): scale on high S spalled only in moist O_2/N_2
- 1999, PWA1480, 1484, CMSX4 (Janakiraman, Meier, Pettit, **Pitt**): spallation for water drop, moist vs dry air
- 2000, FeCrAlY (Tolpygo, Clarke, **UCSB**): delayed scale buckling in air
- 2003, René N5 (Maris-Sida, Meier, Pettit, **Pitt**): spallation in high $\text{P}_{\text{H}_2\text{O}}$ air for high sulfur alloy



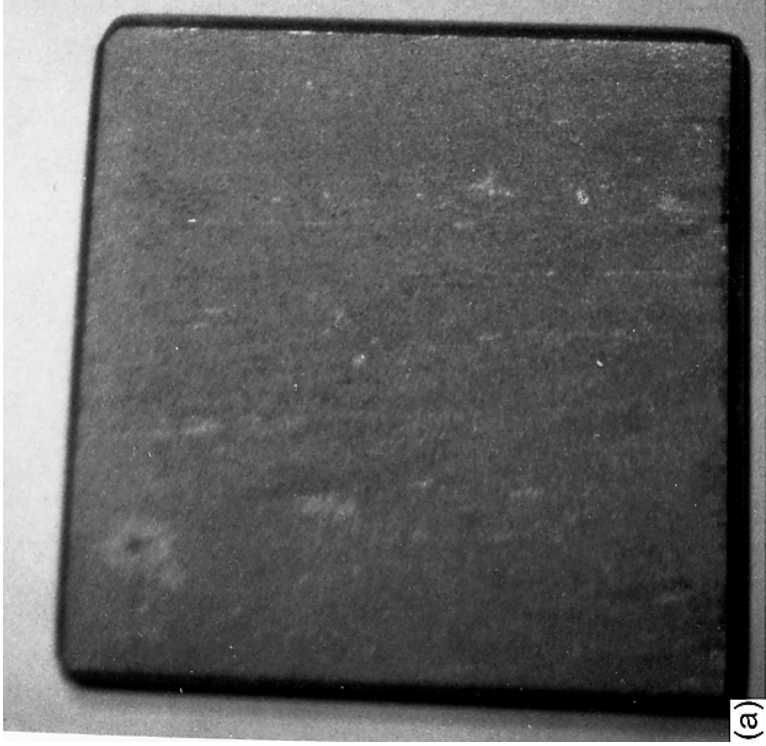
Delayed TBC Failure (Weekend Effect, Desk Top Spallation)

- René N5: TBC buckling growth, moisture-assisted subcritical Al_2O_3 –bondcoat cracks (1997, Clarke, Christiansen, Tolpygo) (1998, Sergo, Clarke)
- CMSX4: progressive scale debond, TBC failure (2000, Peng, Clarke)
- PWA 1484: ‘no bond coat’ TBC delamination, H_2O immersion (1998, ‘02, ‘04, Smialek)

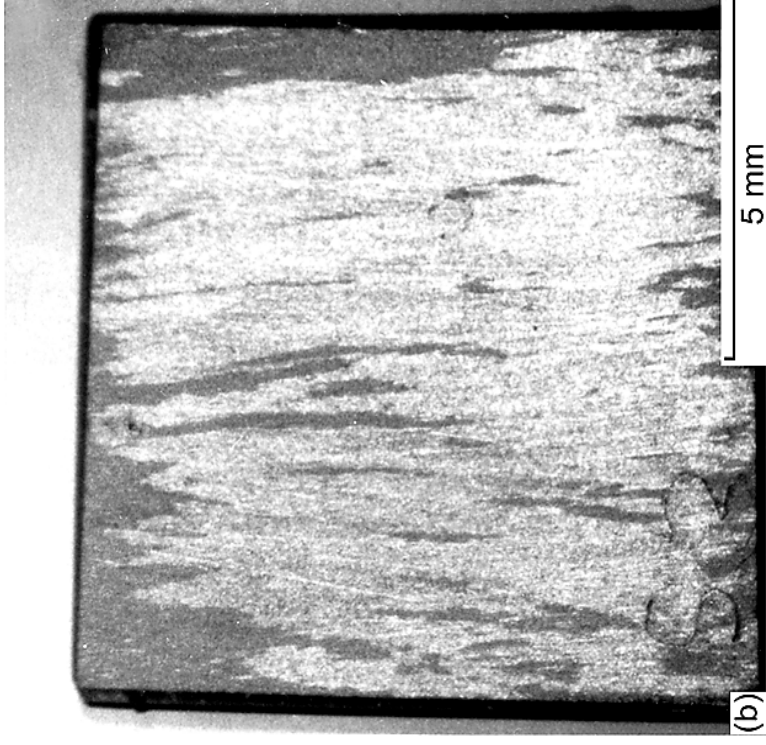


Undoped Ni15Cr13Al, Immersion Effects 15 purging cycles, 1120°C, 1-hr

As-cooled



After water immersion





No Effect of Water Immersion on H₂-Annealed Sample

0.01 ppmw S PWA 1484, 1250°C/50 hr Anneal,

1100°C Cyclic Oxidation (10x)

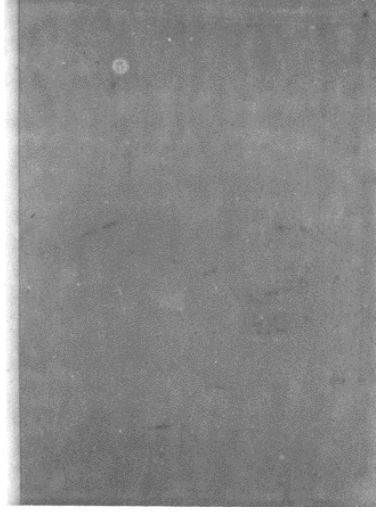
200 hr



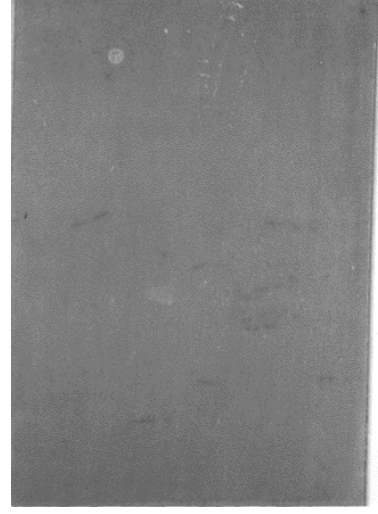
↓ 400 hr + H₂O



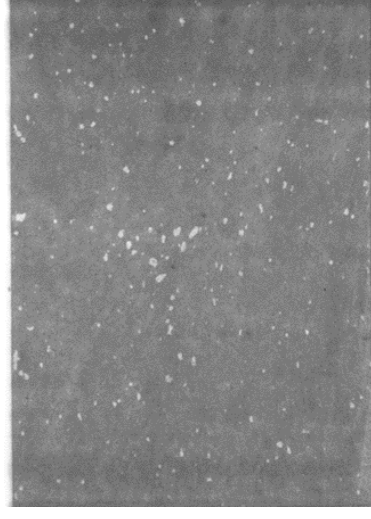
800 hr



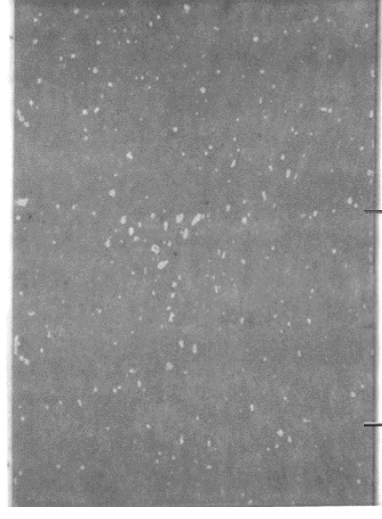
↓ 800 hr + H₂O



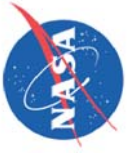
2000 hr



↓ 2000 hr + H₂O



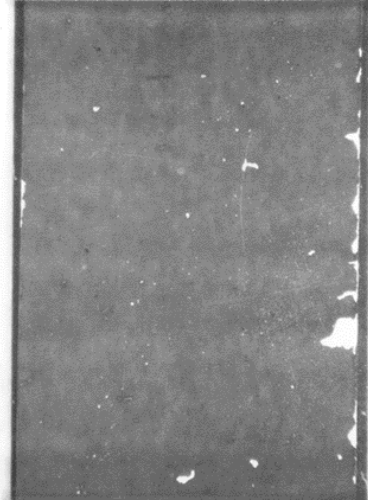
5 mm



Water Immersion Produces Scale Spallation to Bare Metal

Higher S (1.2 ppmw S) PWA 1484, 1100°C Cyclic Oxidation

200 hr



↓ 400 hr + H₂O



800 hr



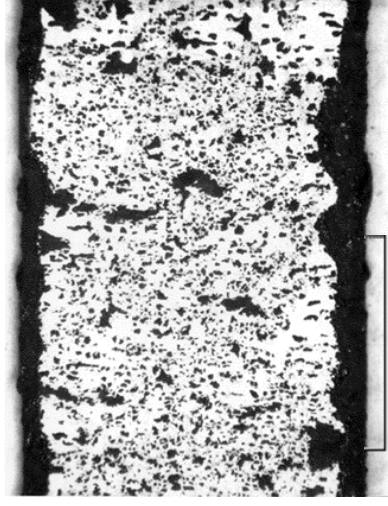
↓ 800 hr + H₂O



2000 hr



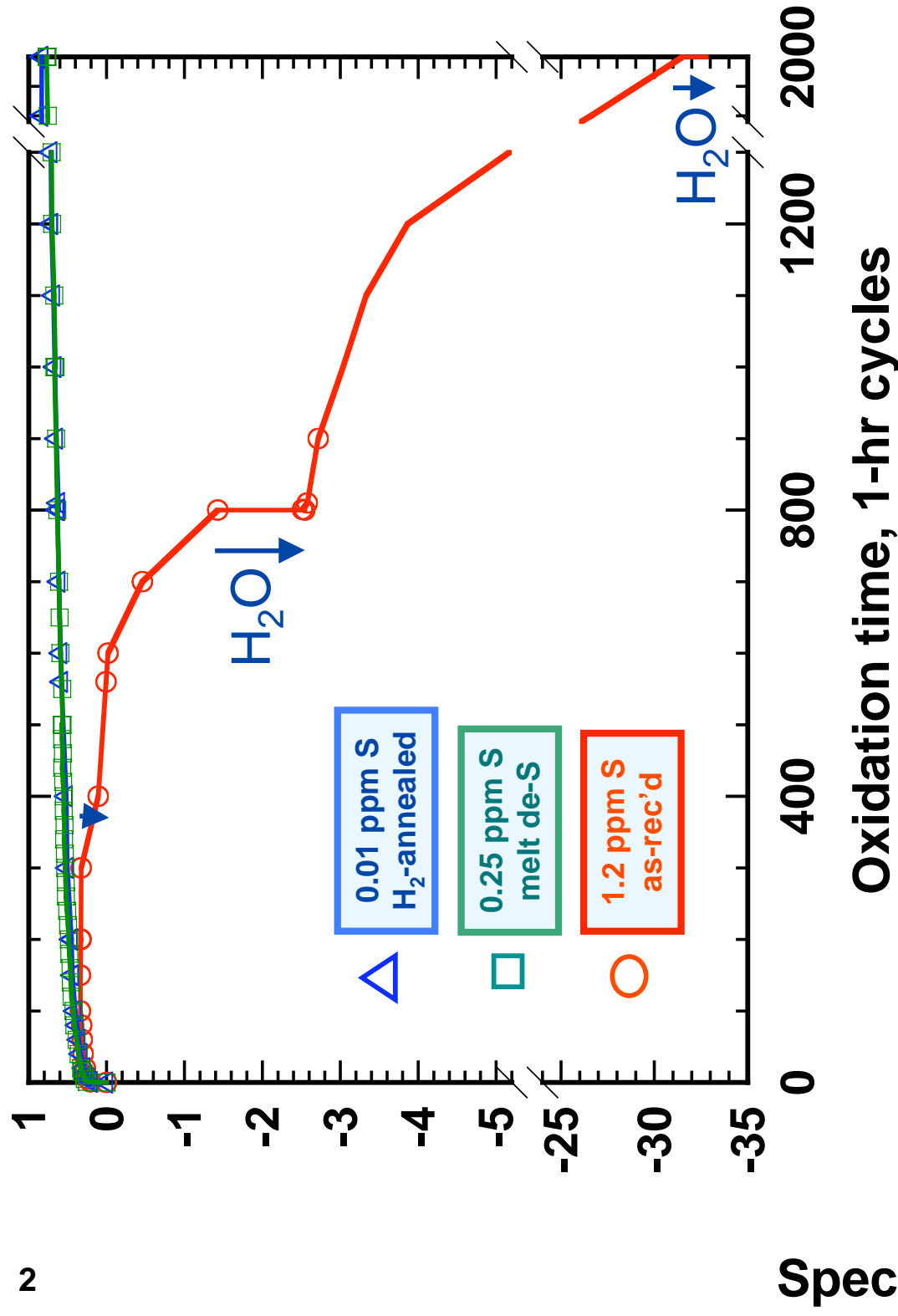
↓ 2000 hr + H₂O



5 mm

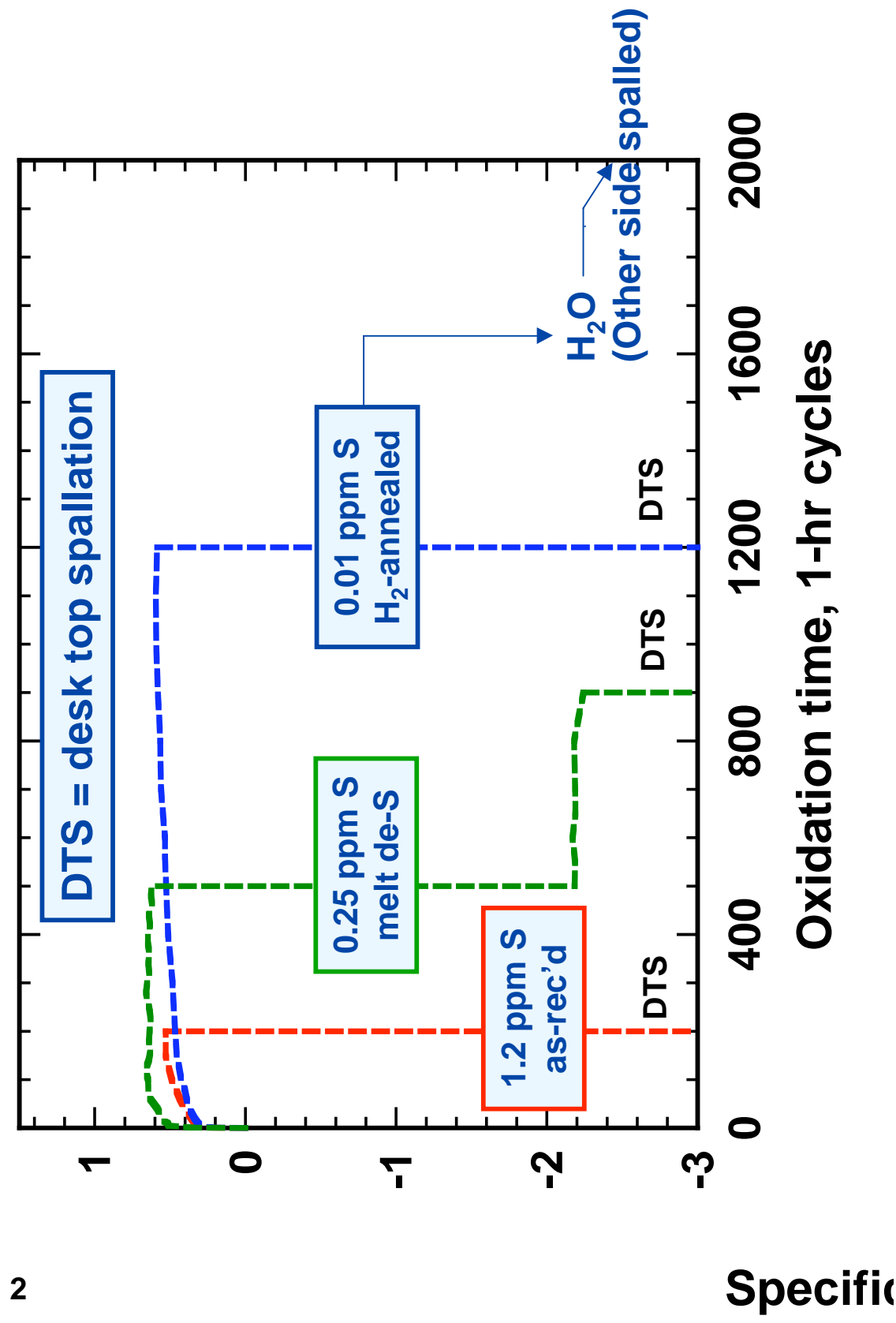
Effect of Sulfur Content on Cyclic Oxidation

PWA 1484 at 1100° C



Effect of Sulfur Content on PS NBC TBC Life

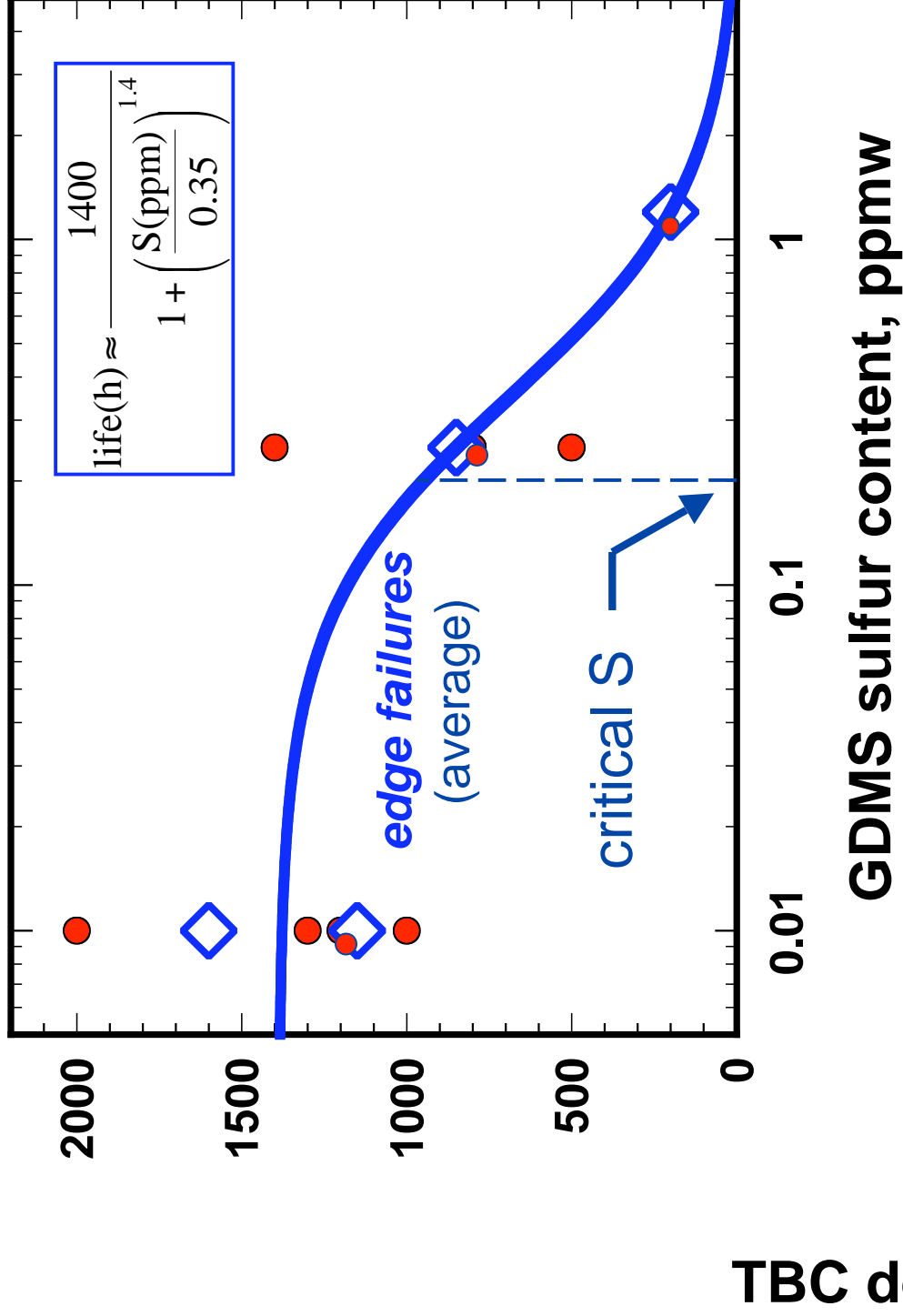
PWA 1484 Cyclic Oxidation at 1100°C





Effect of Sulfur Content on TBC Life

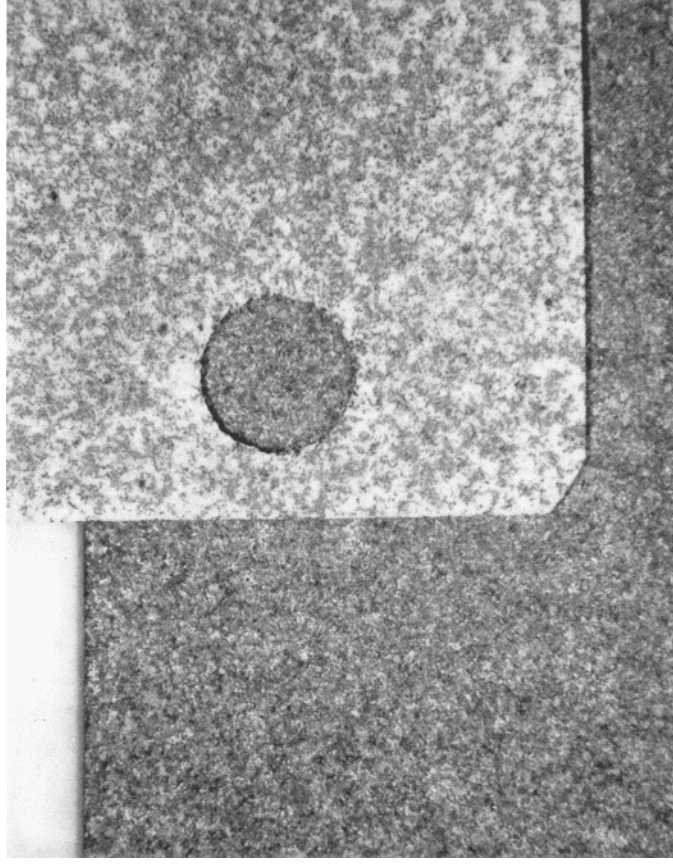
PWA 1484, no bond coat, cyclic oxidation at 1100°C



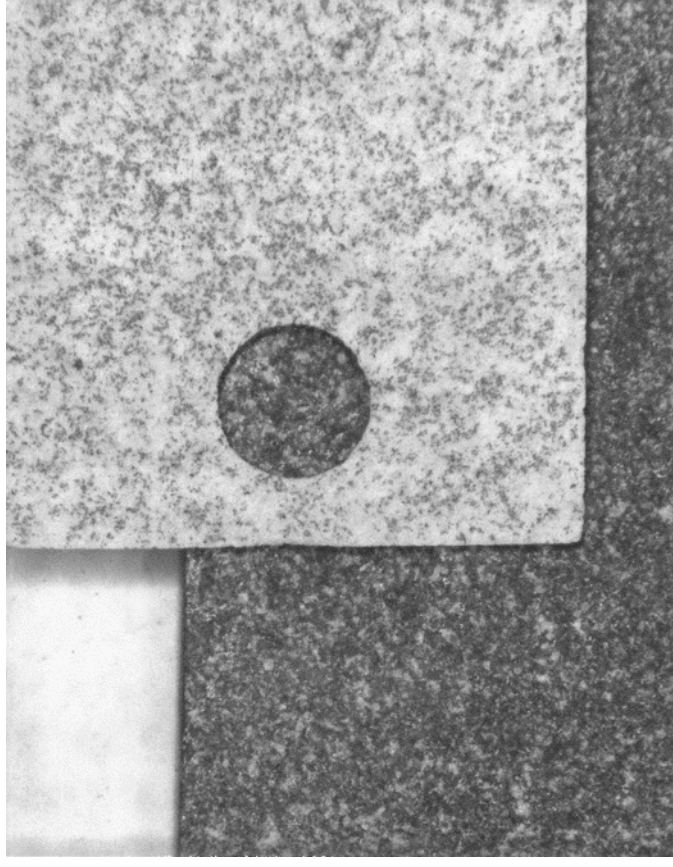


**Substrate and TBC Interface After Delamination (DTS)
High S 1484, no bond coat, 200 hr, 1100 °C Cyclic Oxidation (10x)**

First side sprayed

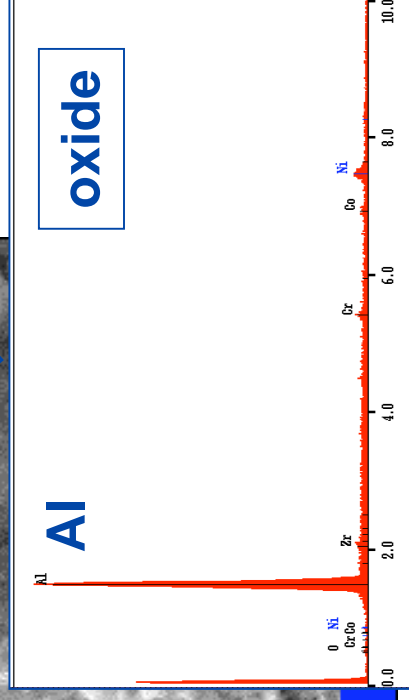
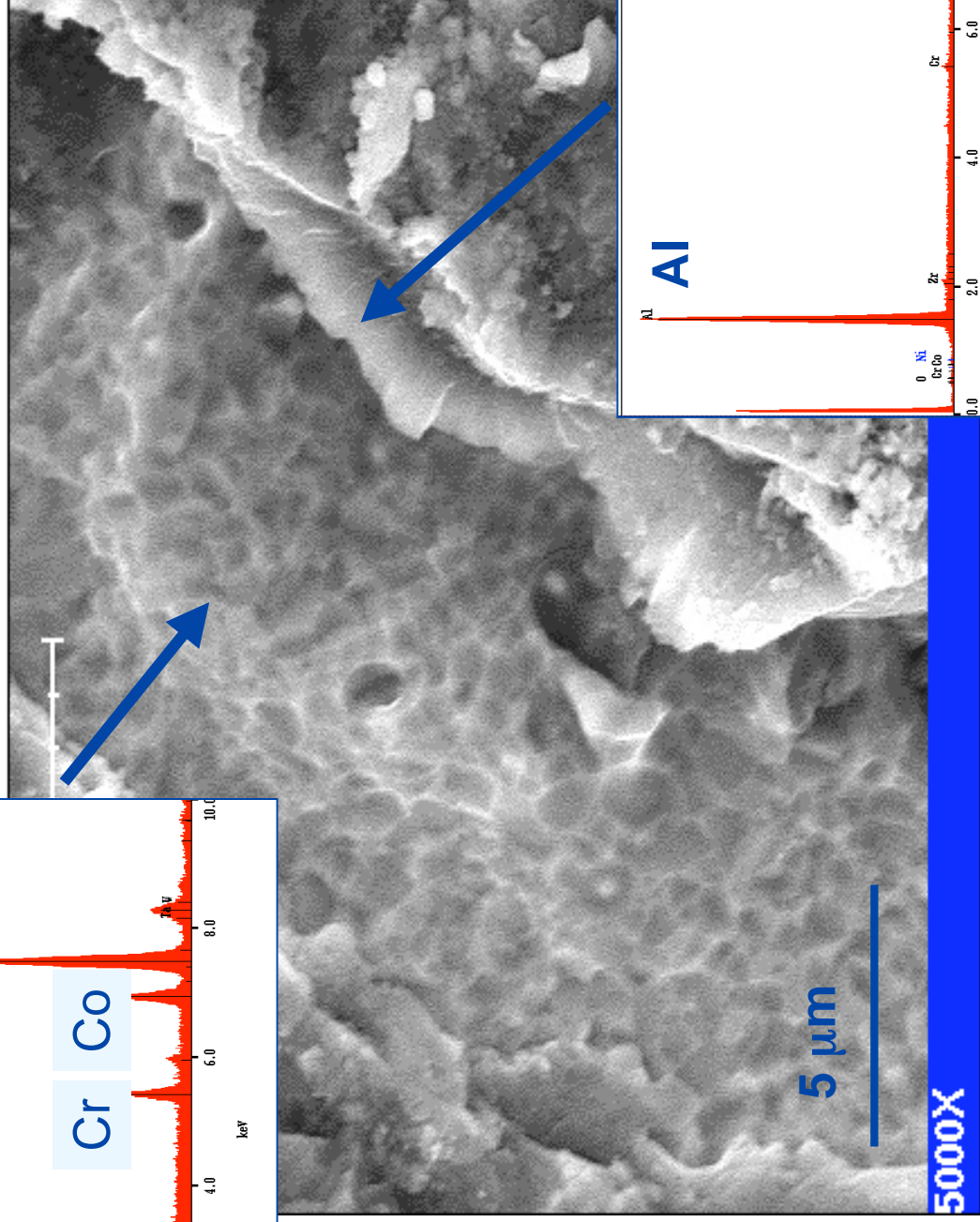
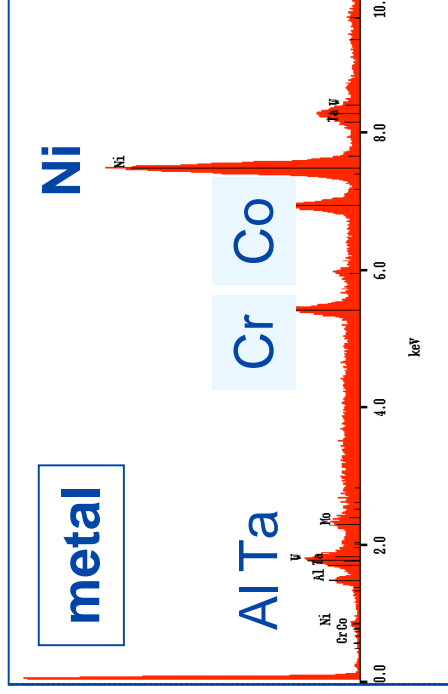


Second side sprayed



5 mm

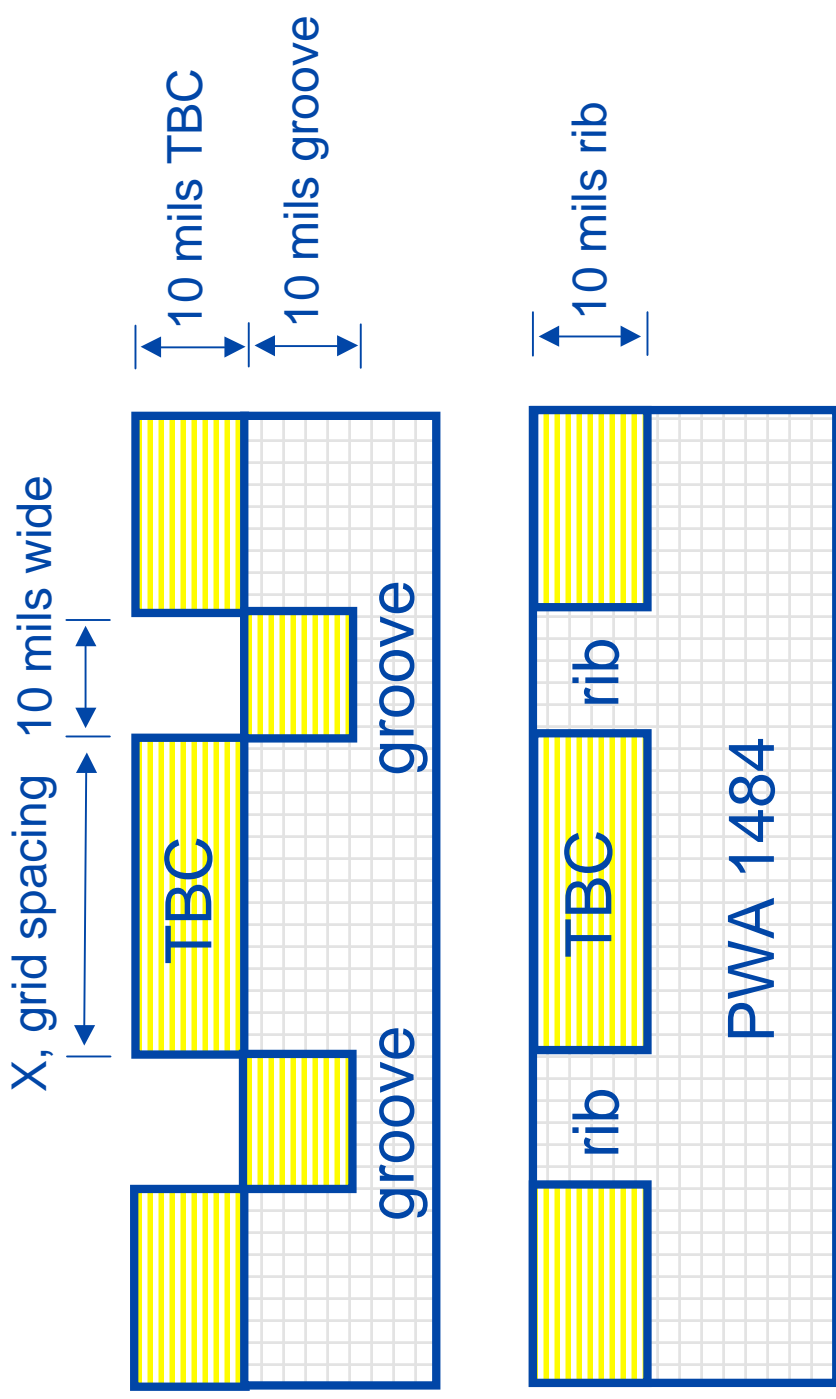
Overnight Interfacial TBC Failure
Hi S 1484; NBC, 1100°C, 200 hours

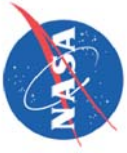




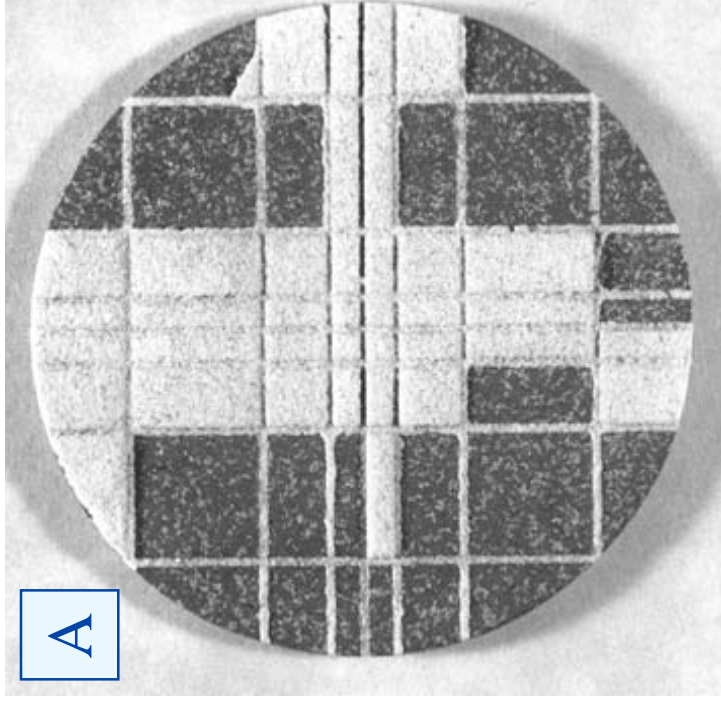
Idealized Schematic Cross-Sections

(not to scale)

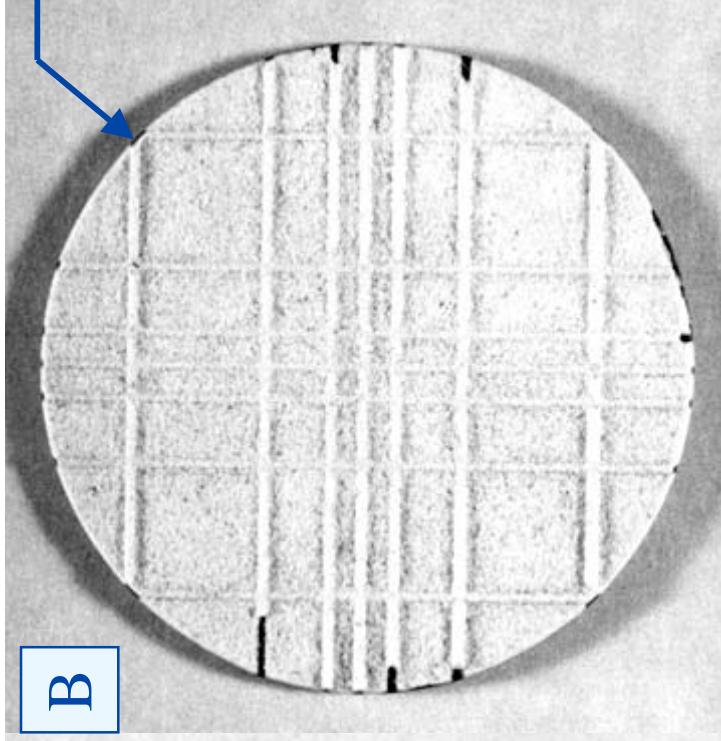




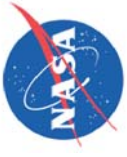
Effect of Segmenting by Grooves and Ribs on TBC Durability (1100°C for 2000 h)



10 mil deep groove pattern
0.050-0.200" spacing
(vs 200 hr flat side)



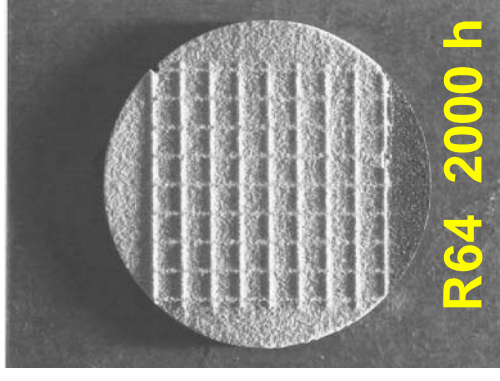
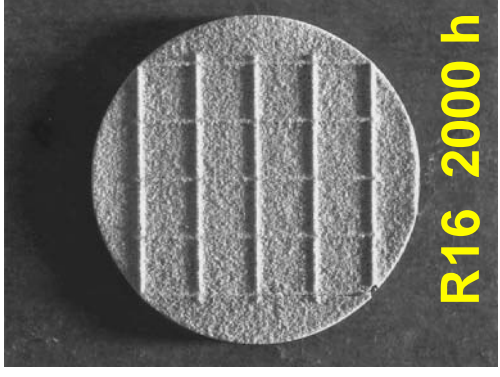
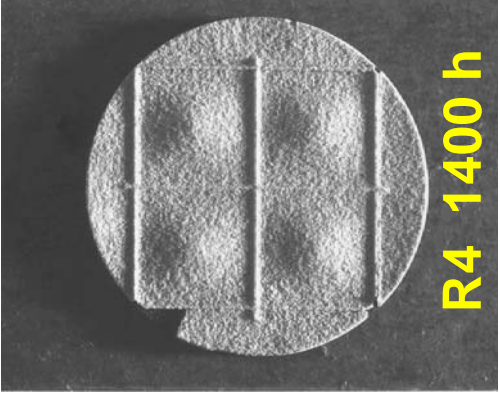
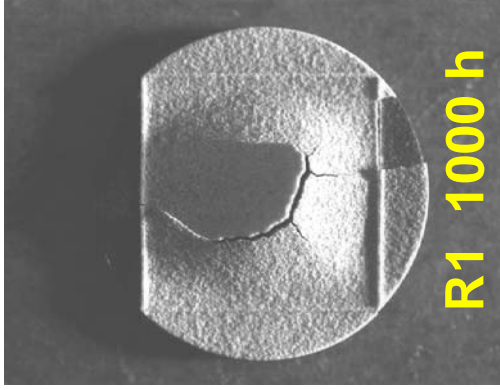
10 mil high rib pattern,
0.050-0.200" spacing
(vs 150 hr flatside)



Segmented TBC Prevents Failure

U.S. Patent 6,316,078; Nov. 13, 2001

Plasma Sprayed 8YSZ TBC, No Bond Coat, Low Sulfur PWA 1484
10 mil Ribs, 1 in. dia.; Interrupted Oxidation Testing at 1100° C



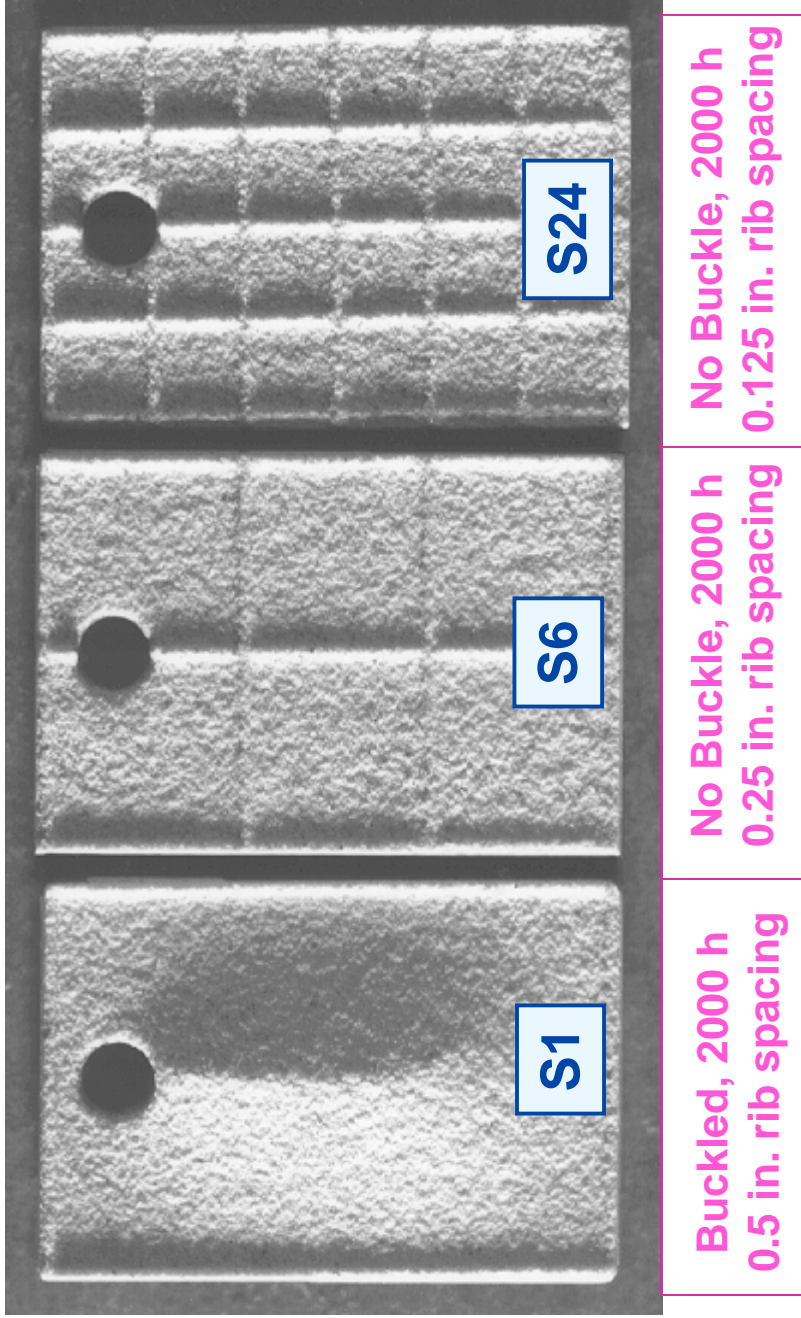
Flat sides (no ribs) delaminate completely at 400-1000 h



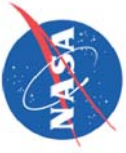
Segmented TBC Prevents Failure

U.S. Patent 6,316,078; Nov. 13, 2001

Plasma Sprayed 8YSZ, No Bond Coat, Low Sulfur PWA 1484
1100°C Cyclic Oxidation, 2000 1-hr Cycles

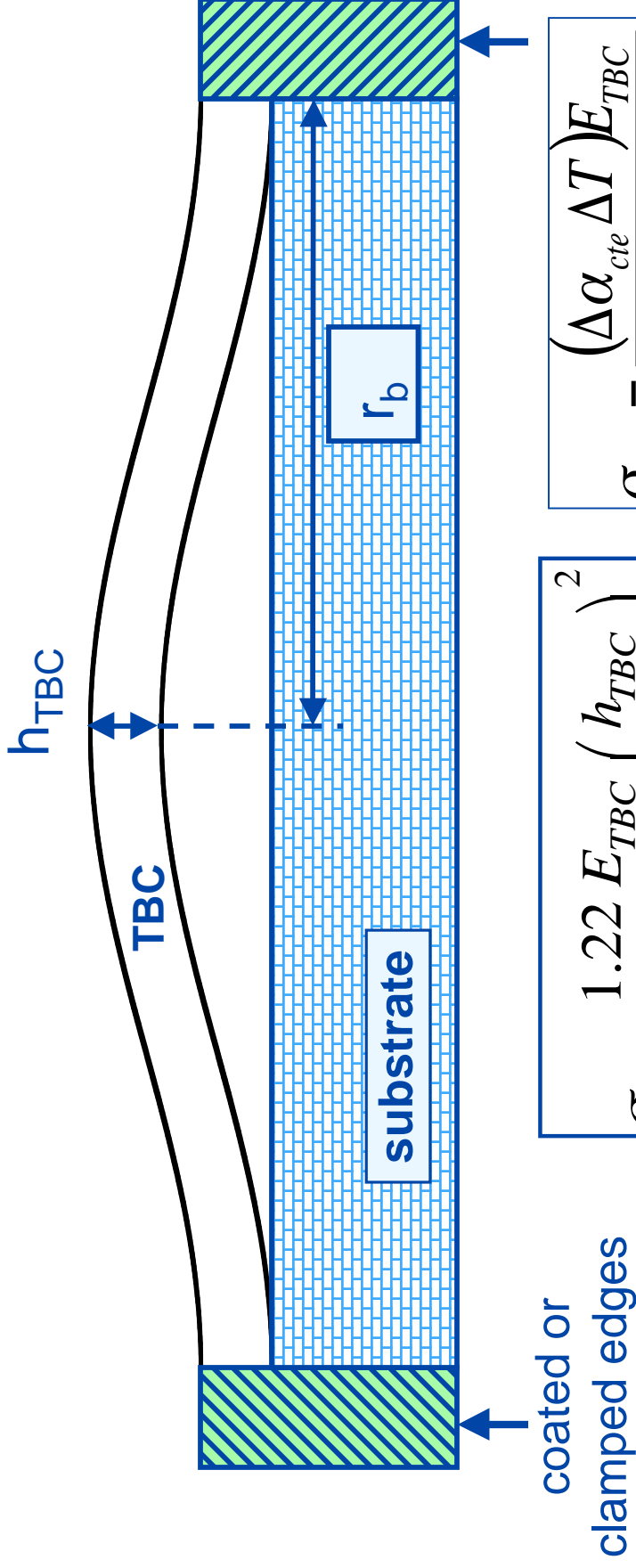


Flat sides (no ribs) delaminate completely at 400-1000 h



Schematic of TBC (Scale) Buckling Failure

(after H. Evans or A. Evans, et al.)



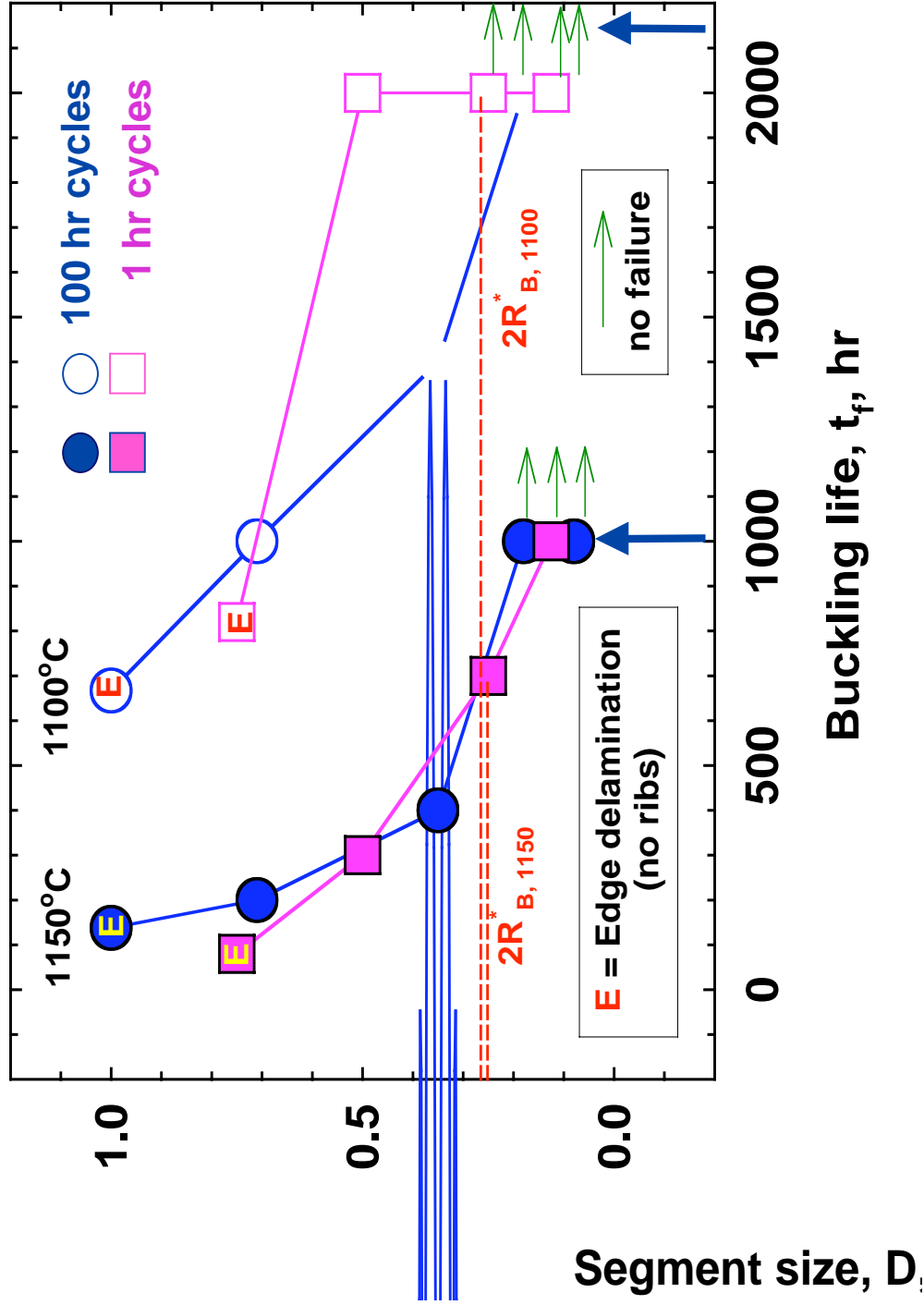
$$\sigma_b = \frac{1.22 E_{TBC}}{1 - \nu^2} \left(\frac{h_{TBC}}{r_b} \right)^2$$

$$\sigma_{cte} = \frac{(\Delta \alpha_{cte} \Delta T) E_{TBC}}{(1 + R)(1 - \nu_{TBC})}$$



Effect of Ribbed TBC Segment Size on Life

10 mil 8YSZ, No Bond Coat, Low S PWA 1484



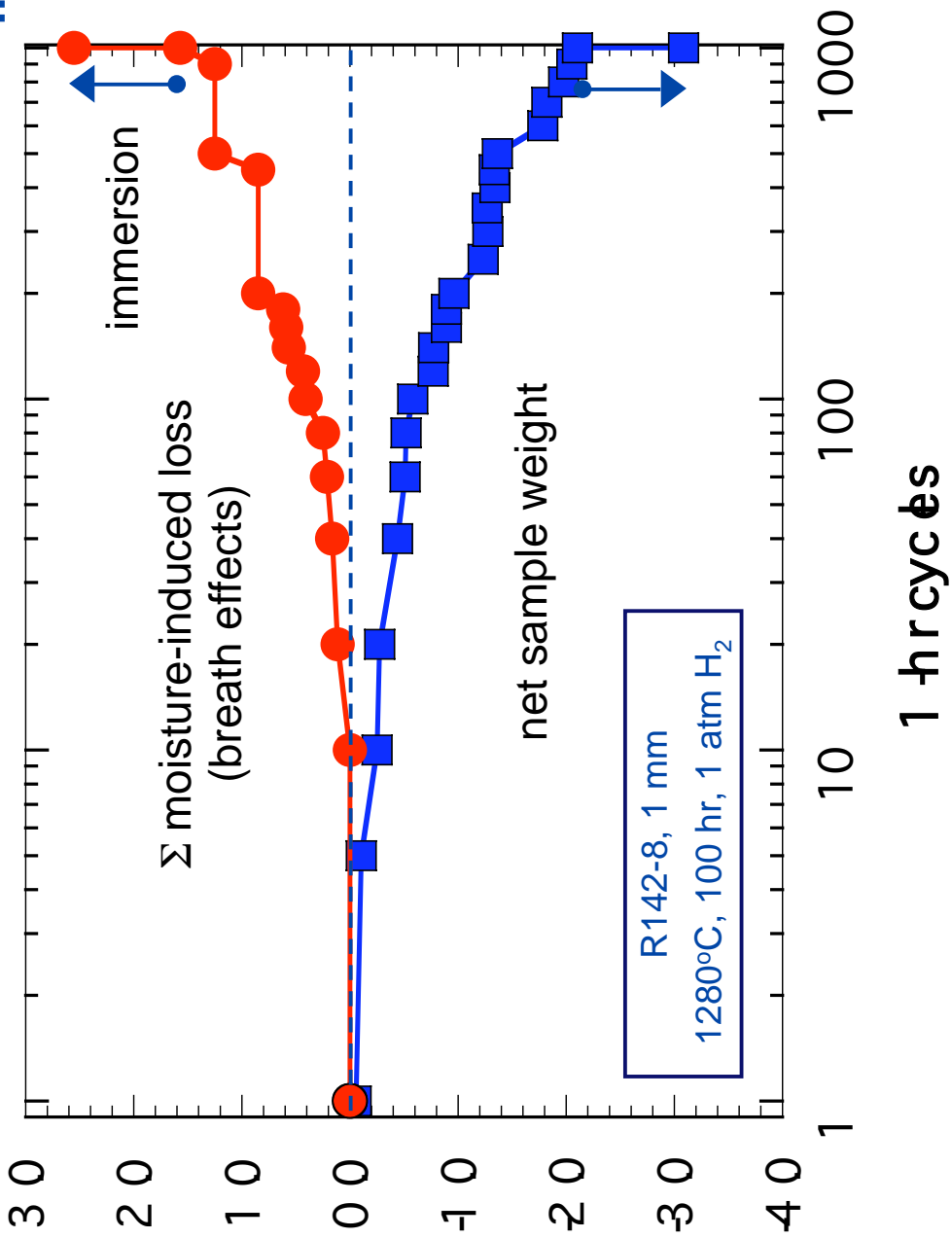
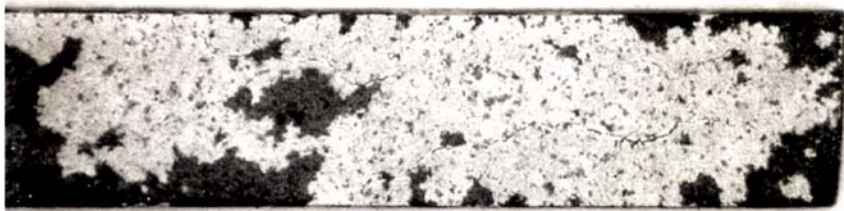


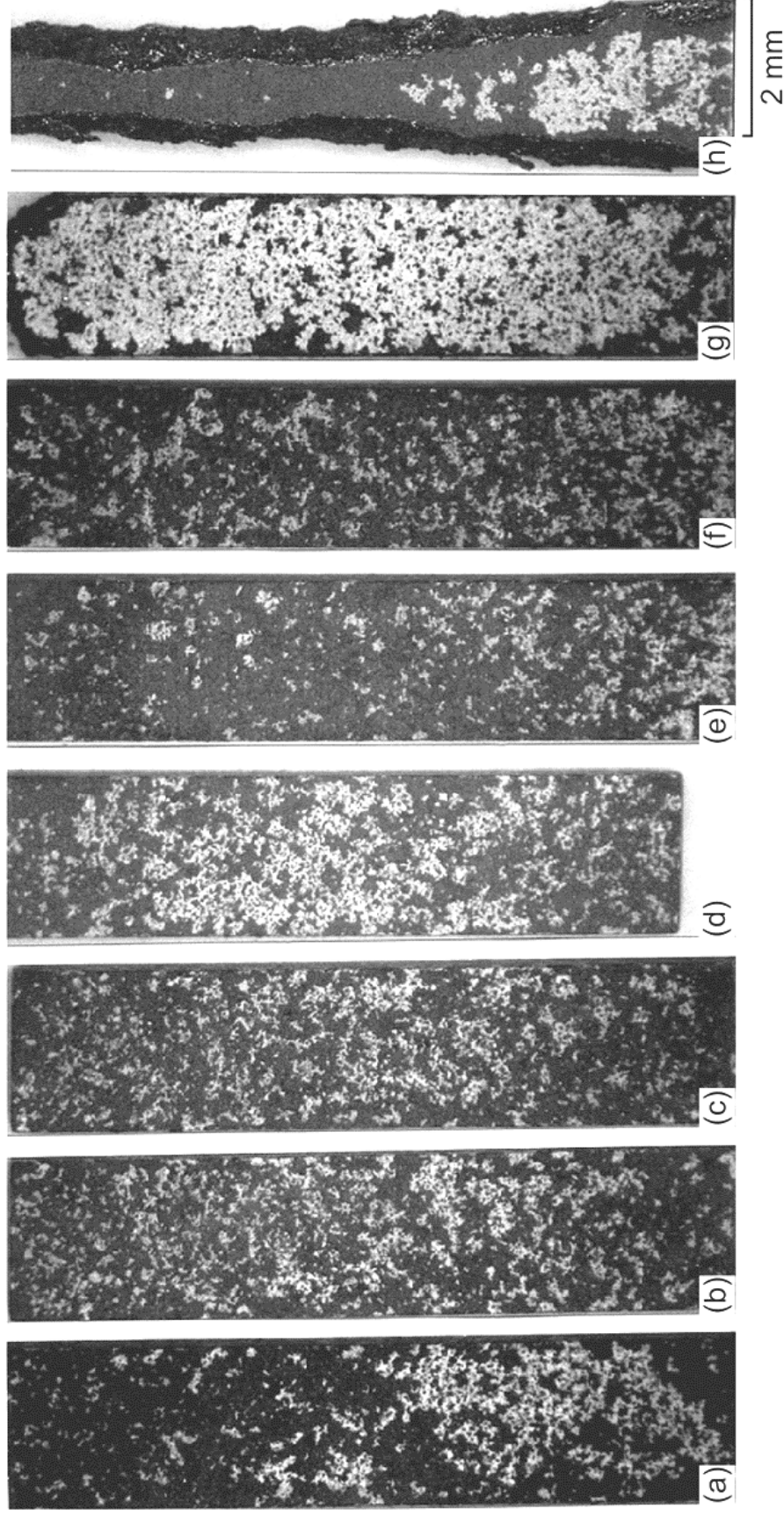
Effect of Moisture Exposure after Cyclic Oxidation of Rene 142 at 1150

as-cooled

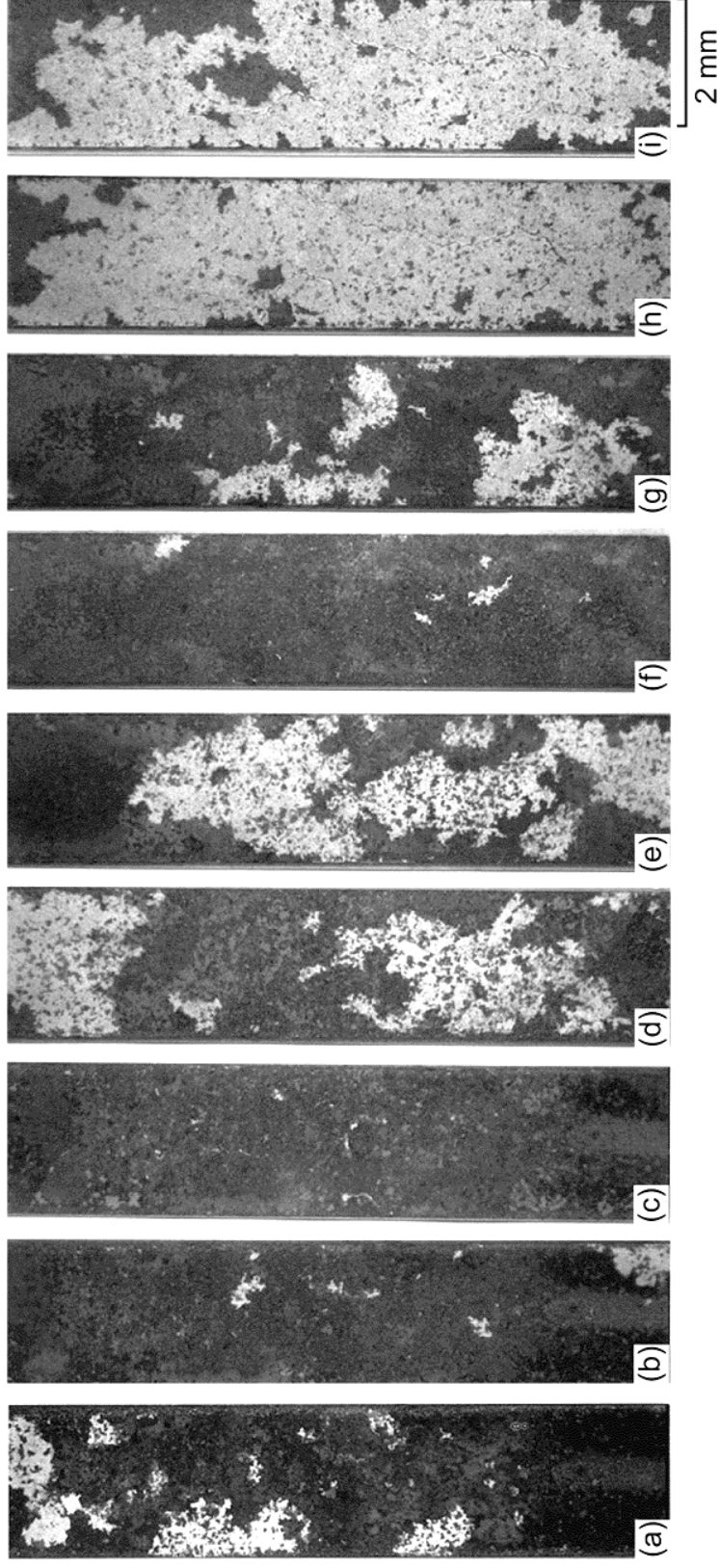


immersed

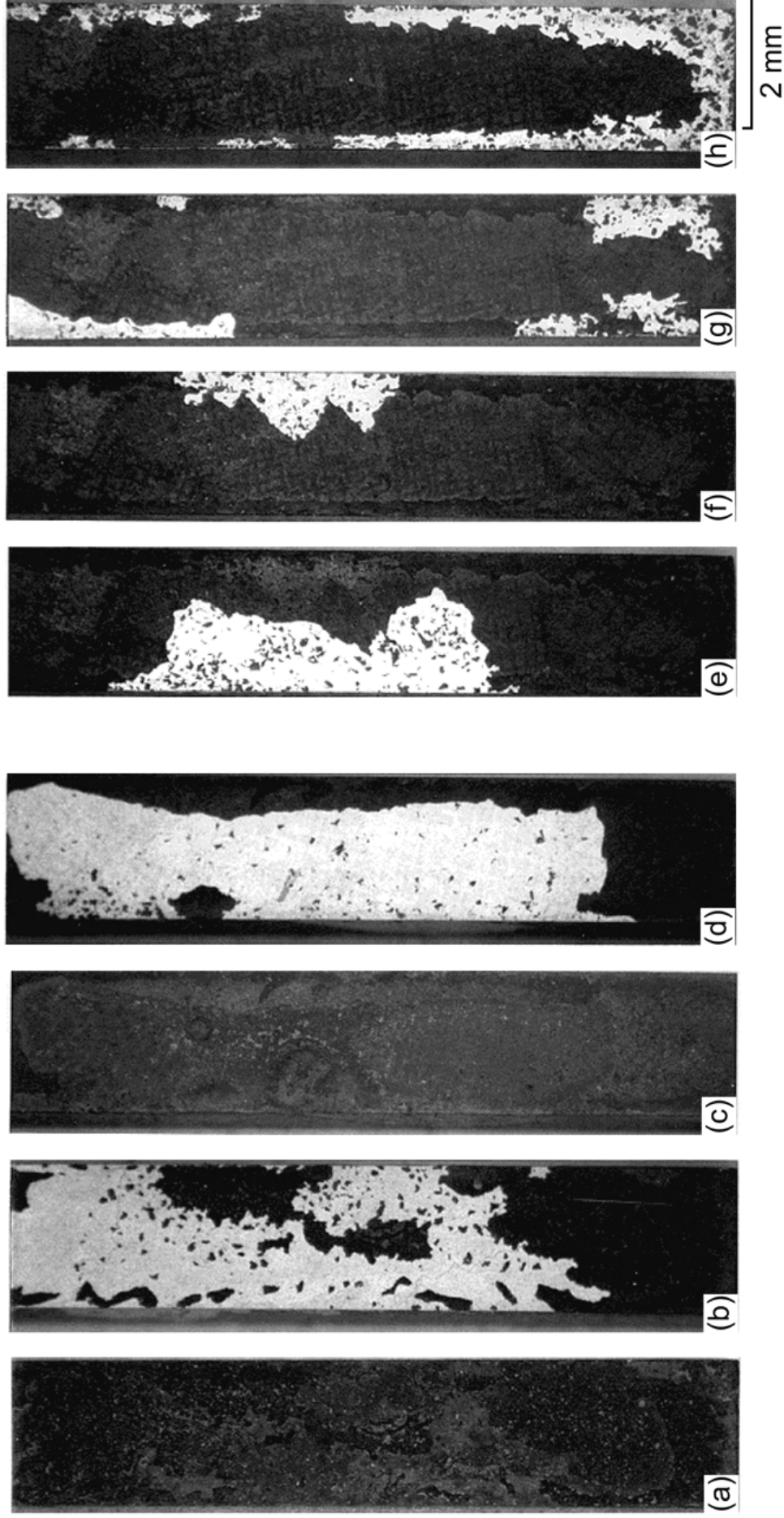




Interfacial spalling for 1150 °C oxidation of as-received René 142. No anneal; moisture treatment (R142-6, 1 mm, 6.1 ppm S). (a) 40 hr. (b) 80 hr. (c) 100 hr. (d) 140 hr. (e) 180 hr. (f) 200 hr. (g) 500 hr. (h) 1000 hr.

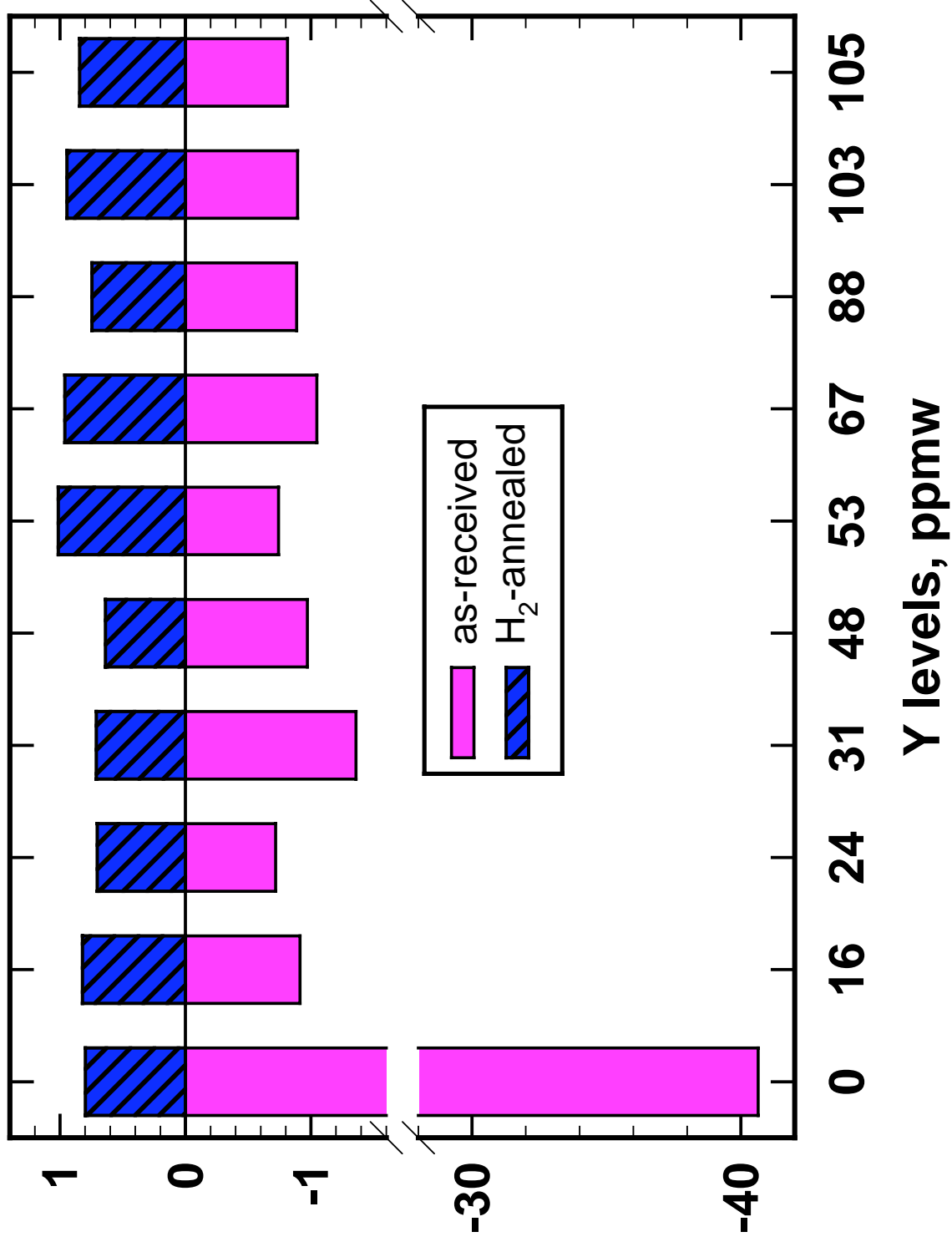


Interfacial spalling for 1150 °C oxidation of annealed René 142. 1280 °C/100 hr H/A; moisture treatment (R142-8, 1 mm, 0.3 ppm S). (a) 40 hr. (b) 60 hr. (c) 80 hr. (d) 100 hr. (e) 140 hr. (f) 180 hr. (g) 200 hr. (h) 500 hr. (i) 1000 hr.



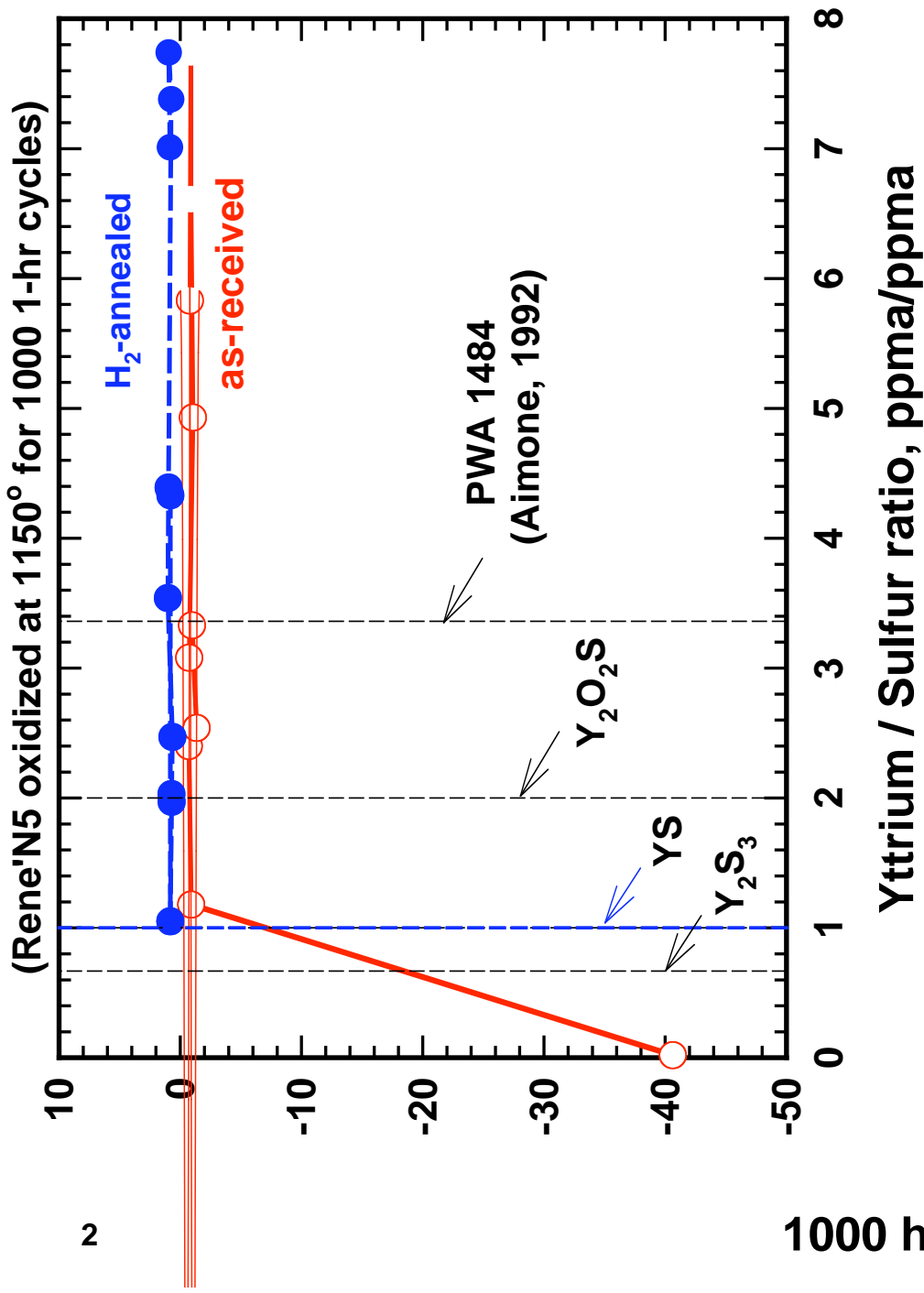
Interfacial spalling for 1150 °C oxidation of annealed René N5 (+Y). 1280 °C/100 hr H/A; moisture treatment (N5-2, 3 mm, 3.7 ppm S). (a) 20 hr, side b. (b) 80 hr, side b. (c) 100 hr, side b. (d) 140 hr, side b. (e) 180 hr, side d. (f) 200 hr, side d. (g) 500 hr, side d. (h) 1000 hr, side d.

Effect Y Content and H₂ Annealing on Final Weight Change (Rene'N5 after 1000 1-hr Cycles at 1150°C)



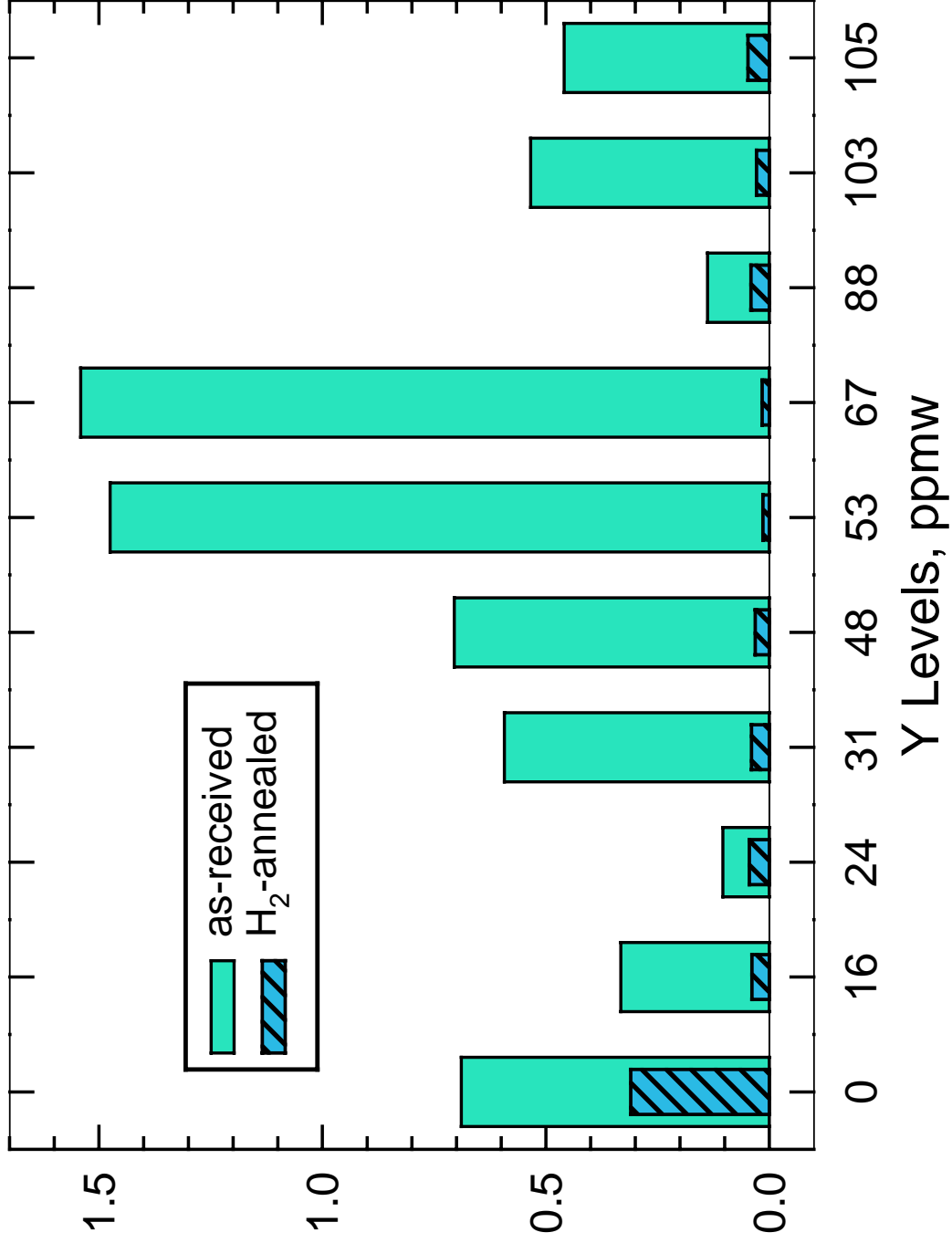


The Effect of Y/S Ratio on Oxidation Behavior



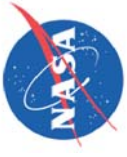


Effect of Water Immersion on Spalling (Rene'N5 after 500 1-hr Cycles at 1150°C)



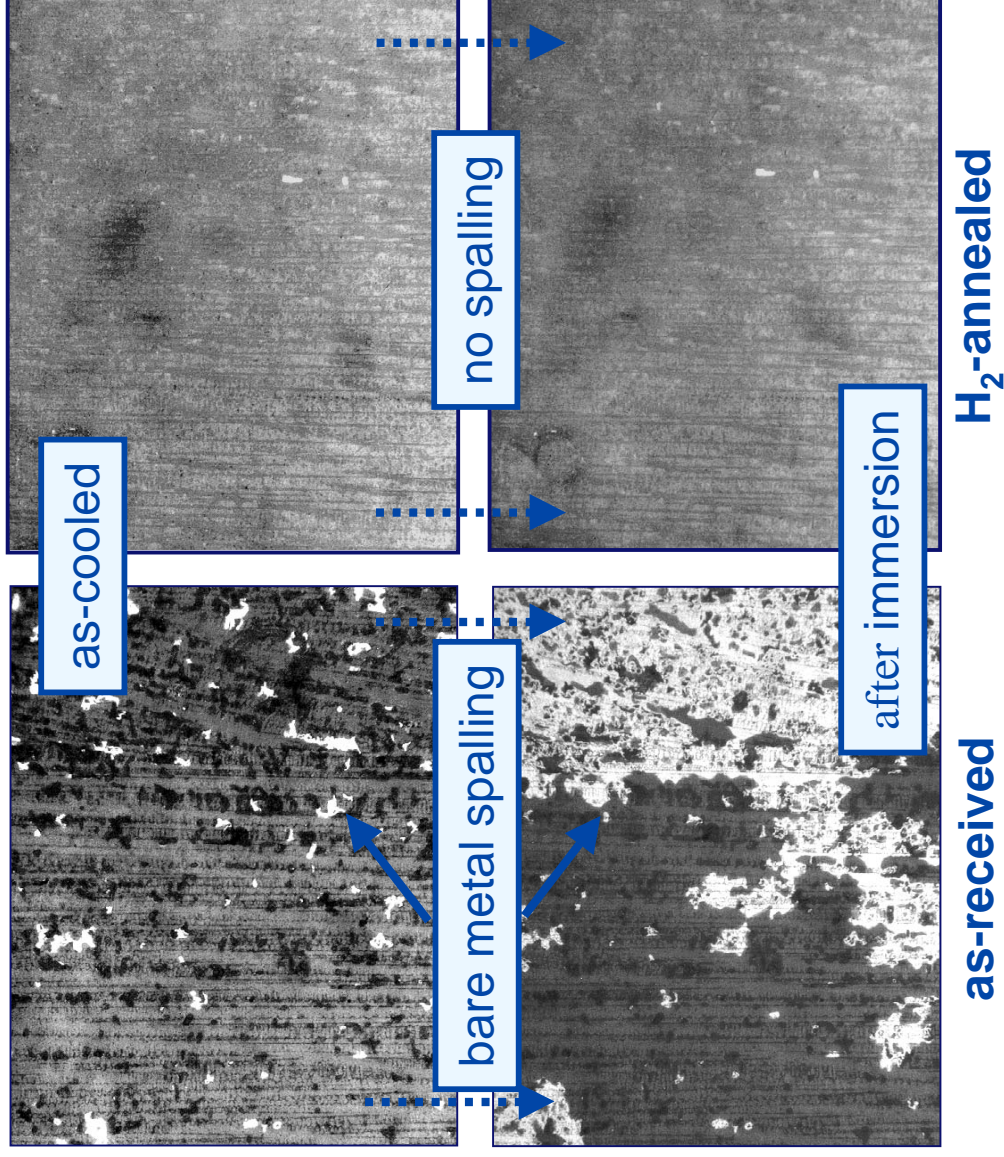
2

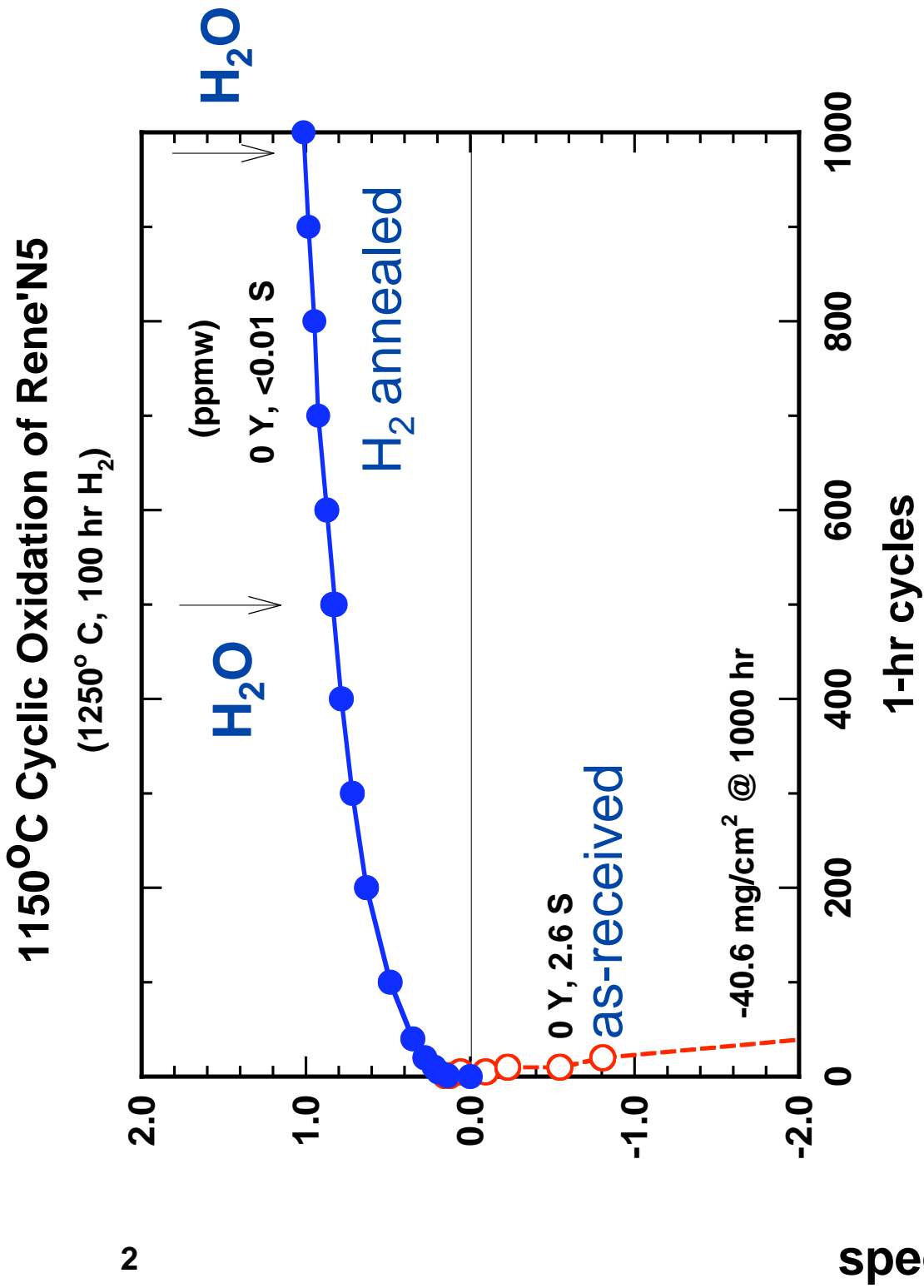
spall due to



Effect of Water Immersion on Spallation

Rene'N5+103Y, 1150°C, 500 hr

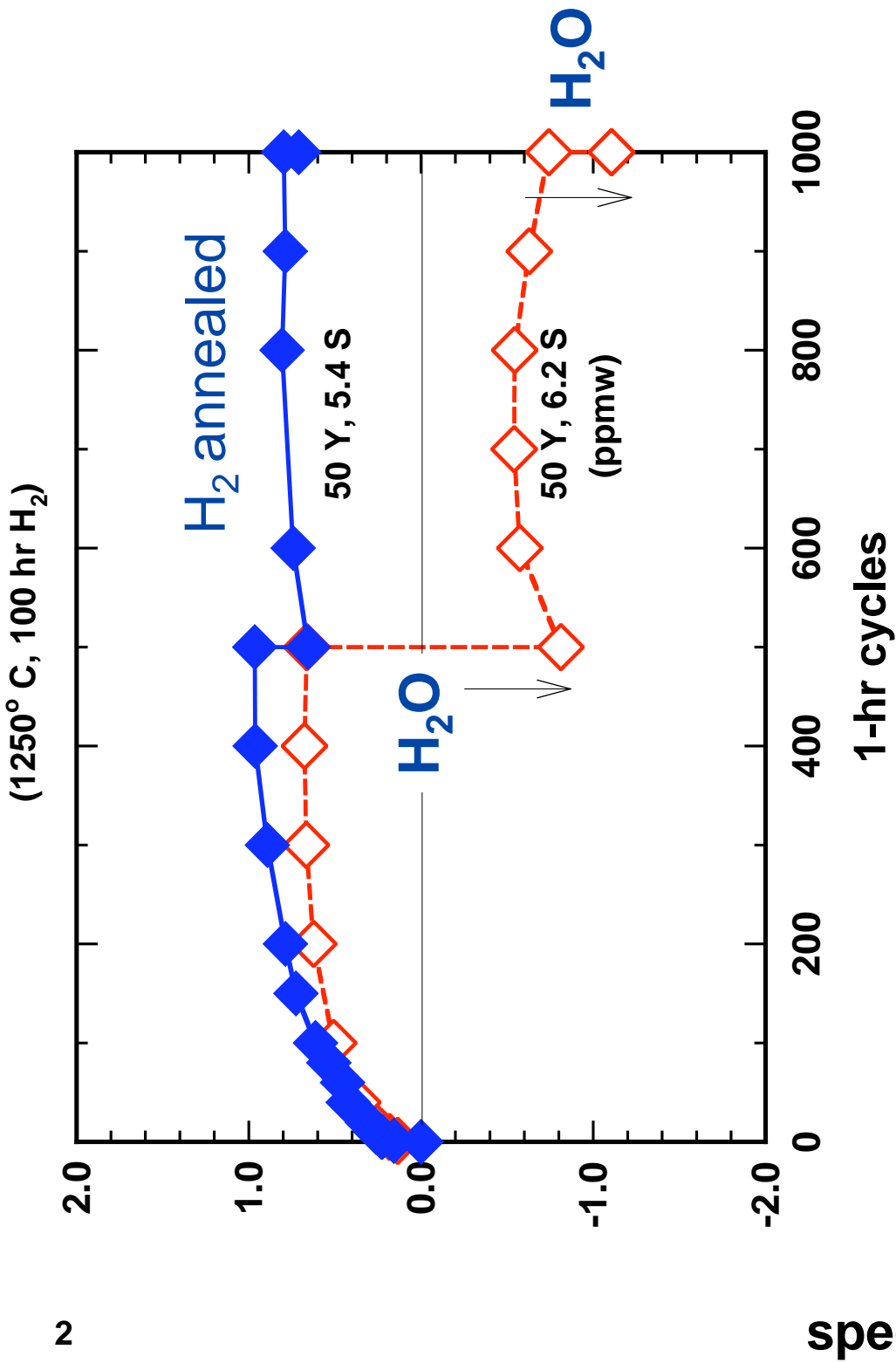


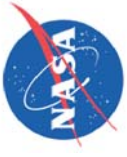




Immersion Effect for Rene'N5 (+Y)

1150°C, 1-hr cycles, $\pm Y$, H-annealing

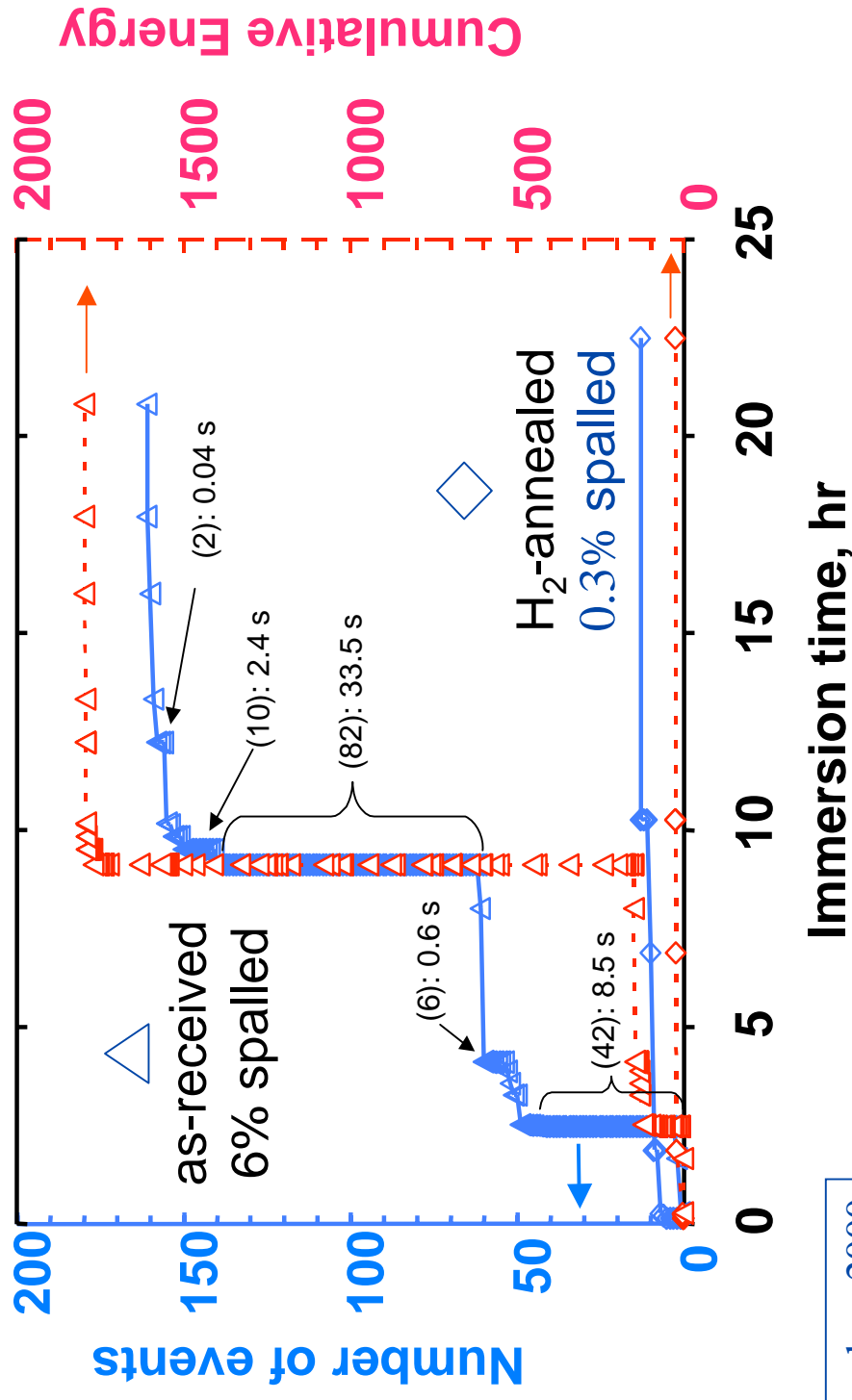




Moisture-Induced Delayed Spallation (MIDS)

Acoustic Emission during Immersion

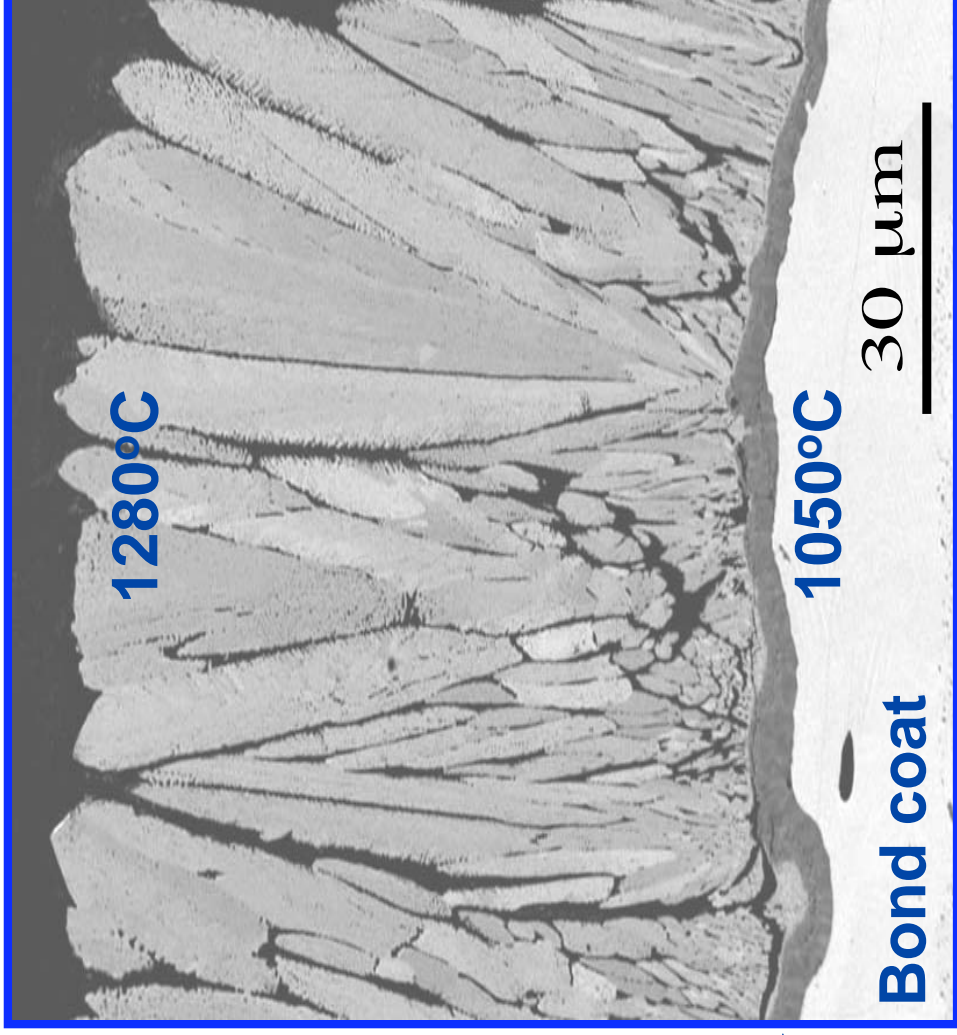
(pre-oxidized Rene'N5+Y, 1000 1-hr cycles @ 1150°C)



G.N. Morscher, 2000



EB-PVD $7Y_2O_3$ - ZrO_2 TBC
Ni(Pt)Al bond coat, Rene'N5,
Laser HHFT, 1280/1050°C, 200x2 hr



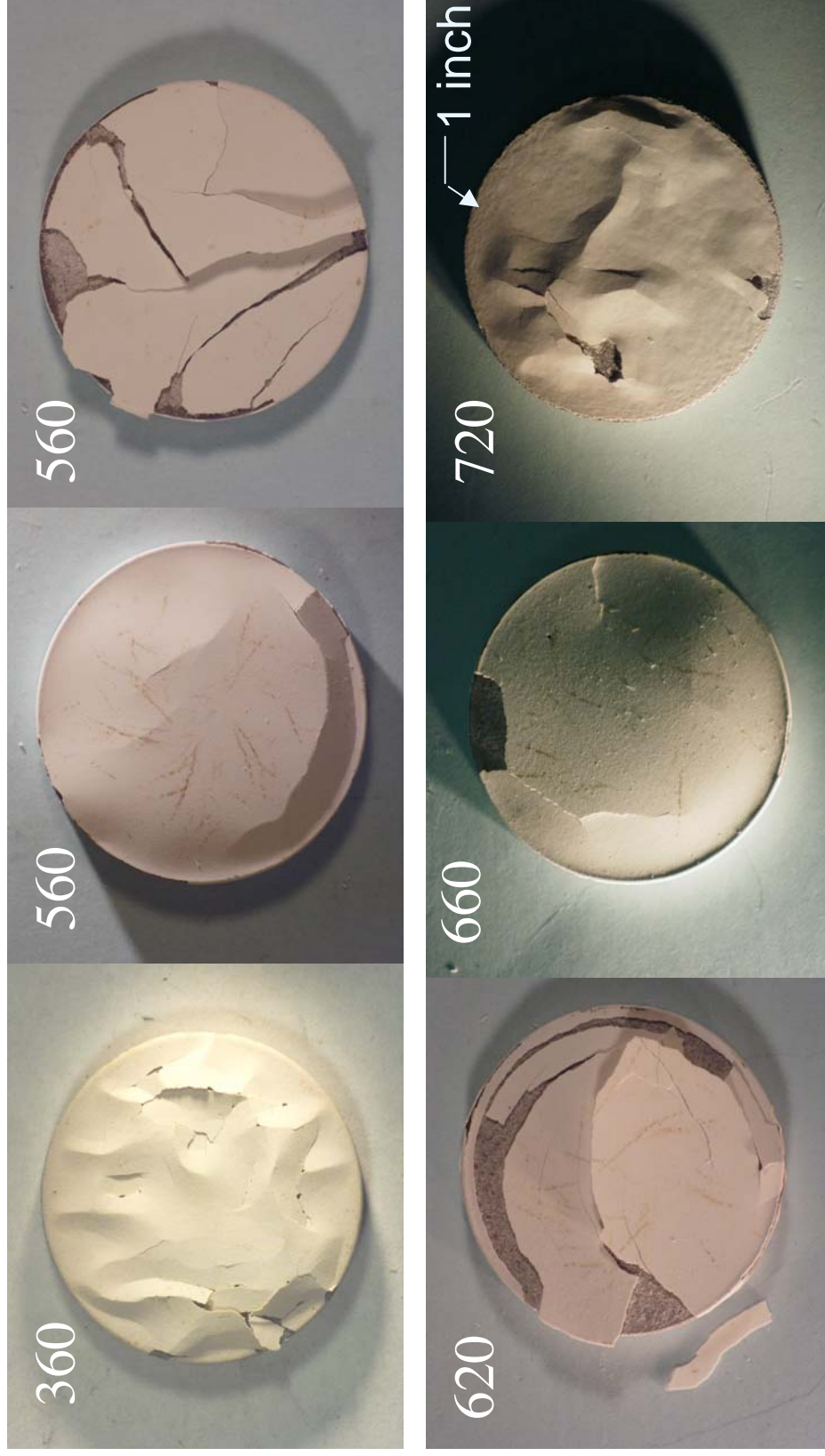
7YSZ

Al_2O_3
scale

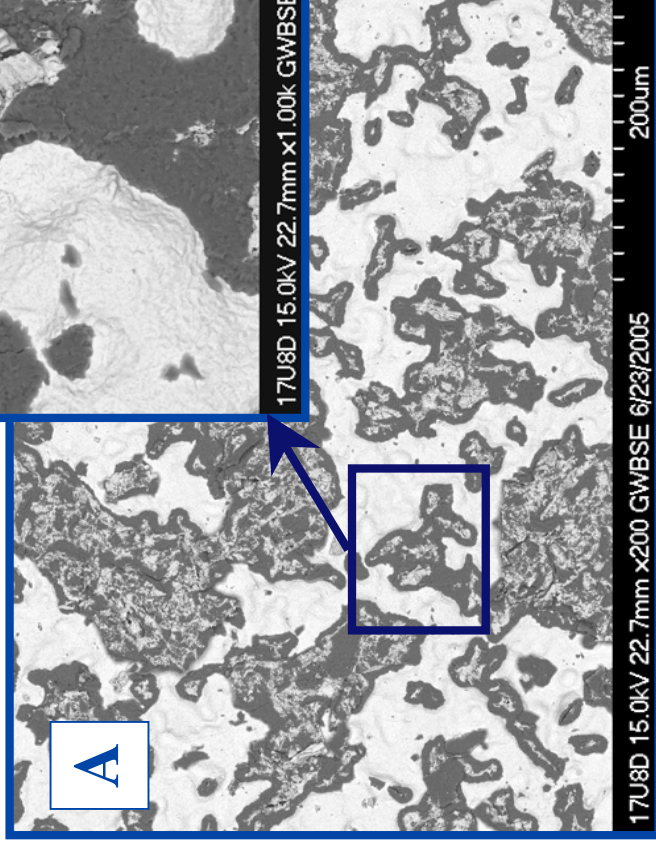
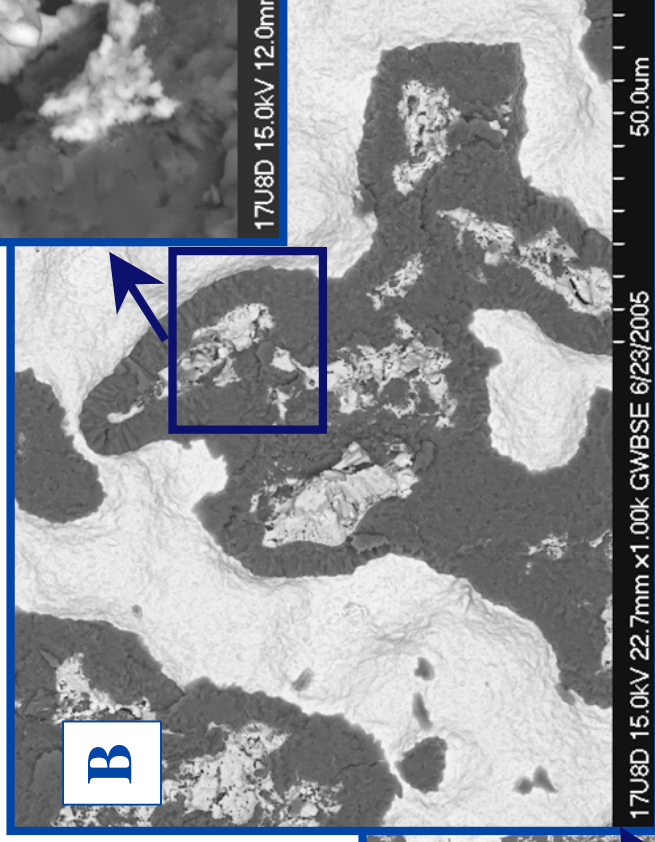
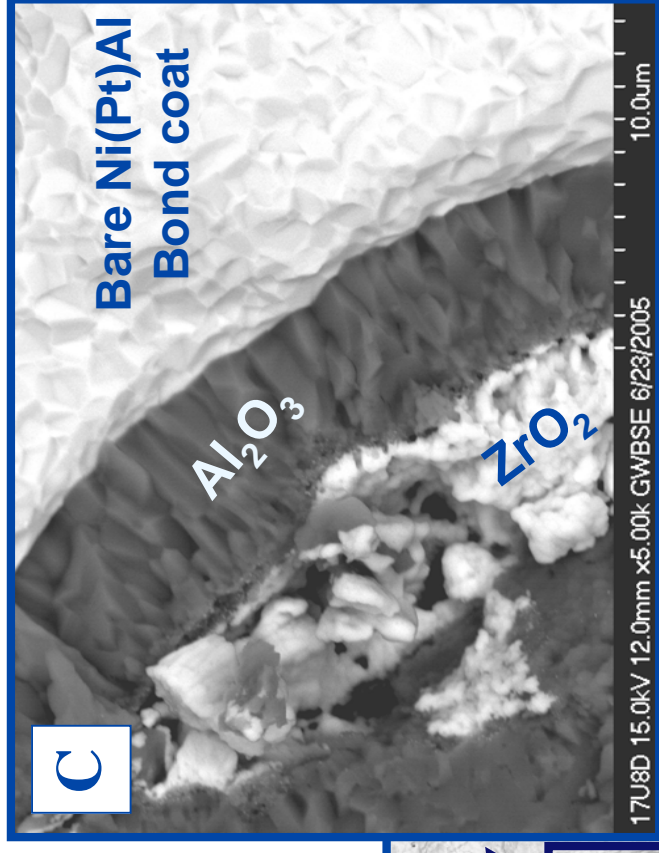
Zhu, 2001



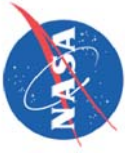
Delayed Desk Top Failures of EB PVD TBC Ni(Pt)Al bond coat on Rene'N5; 1135°C 360-720 cycles to failure; 45 min/ hot cycle



PVD TBC Failure Locus
(Exposed substrate)
560 cycles @1135°C,
200, 1000, 5000x, BSE



A large portion of the TBC failure
is at the scale-metal interface

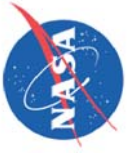


Moisture-Induced Delayed Failure

EB-PVD RE-YSZ, Ni(Pt)Al, Rene N5, 1150°C, 300 cycles



Oct. 10, 2006



Slow (Subcritical) Crack Growth (?)

In bulk Al_2O_3 :

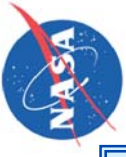
(Weiderhorn, Ritter, Nagabhooshanam, Kotchick, Ebrahimi, 1968-2000)

- $v_c \approx 10^{-6}$ to 10^{-3} m/s
- $\text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} = 2\text{Al}(\text{OH})_3$

For Al_2O_3 scale – NiCrAl interface:

(Acoustic emission, Smialek-Morscher, 2002)

- $v_c \approx 10^{-3}$ to 10^2 m/s
- $\text{Al} + 3 \text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3/2 \text{H}_2$



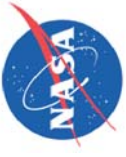
Ambient Moisture-Induced Hydrogen Embrittlement of Intermetallics

(compelling analogy to delayed scale spallation)

- Extrinsicly brittle M_3X compounds:
(Ni,Fe,Co)₃(Al,Si,Ti)
- Embrittled by moist air, not dry O₂, or vacuum:
$$2Al + 3H_2O = Al_2O_3 + 6H^+$$

[or $Al + 3H_2O = Al(OH)_3 + 3H^+$]
- Max effect near room temperature
- Only at slow vs high strain rates

(Stoloff et al., Liu et al.)
1994 MRS Keynote Lecture



Intermittent Nature of Crack Growth in Hydrogen Embrittled High Strength Steel

**“...crack propagation is a discontinuous process...
...further growth must await diffusion of hydrogen...
...the plateaus...are the ‘secondary’ incubation periods...”**

**A.R. Troiano, Chairman, Dept. of Metallurgy
Case Institute of Technology
1959 Edward de Mille Campbell Lecture, ASM**



1960

THE ROLE OF HYDROGEN

65

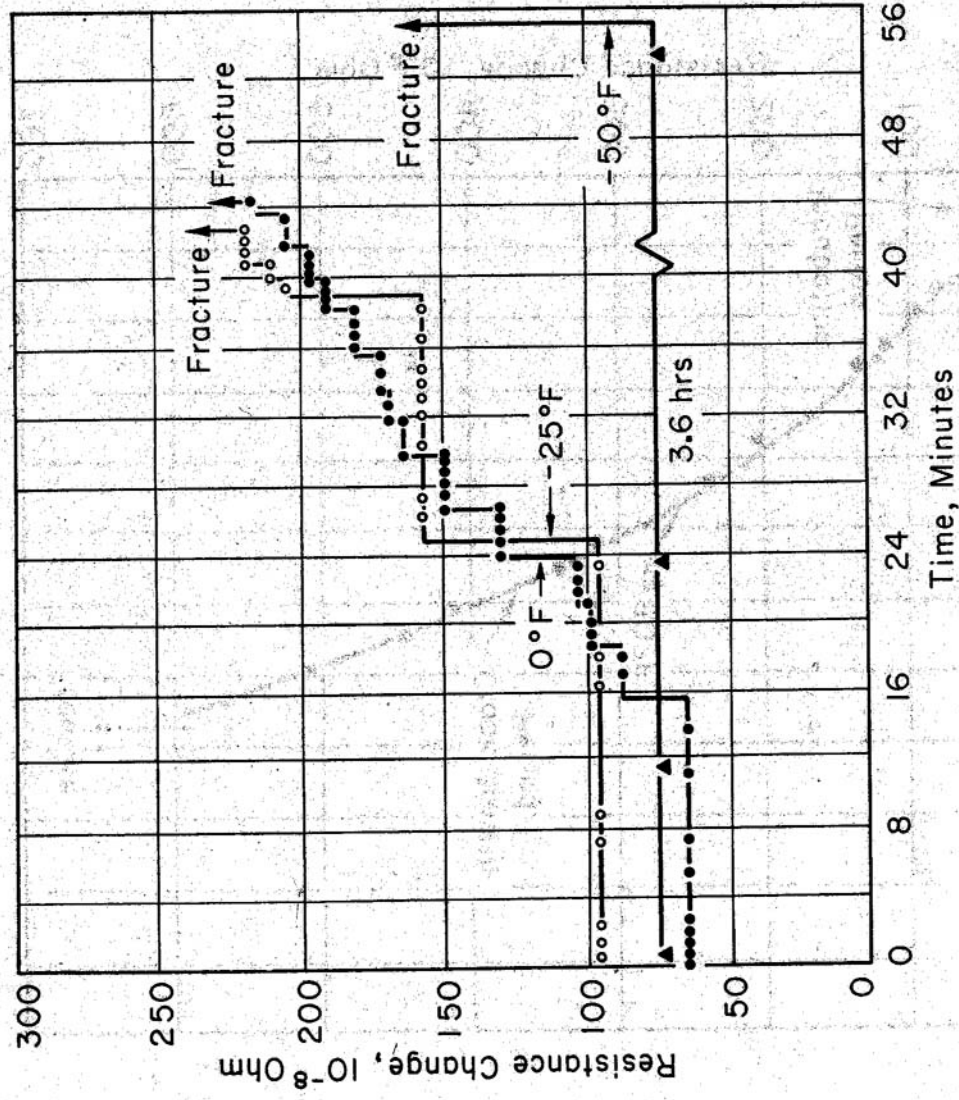
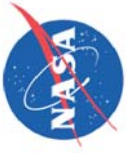


Fig. 11. Resistance Increase as a Function of Time For Uniformly Hydrogenated Specimens Tested in the Stress Range of Delayed Failure (Troiano, 1959)



Hydrogen Embrittlement and Moisture-Induced Delayed Failures

(steels, Ni-alloys, aluminides)

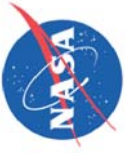
Common Features

Alloy Fracture (1951-1989)

Scale Spallation (1985-2005)

Sulfur segregation	Intergranular embrittlement	✓	Interfacial weakening
Theoretical strength	H, S decrease M-M bond	✓	H, S decrease M-Al₂O₃ bond
Moisture effects,	Intergranular and cleavage	✓	Interfacial weakening
Hydrogen diffusion,	Delayed failure at Rm Temp.	✓	Delayed Rm Temp. failure
Tensile stress state	Intermittent crack growth	✓	Intermittent spallation
H + S segregation	Negative synergy	?	Negative synergy
Cathodic charging	H-embrittlement	?	Interfacial de-scaling

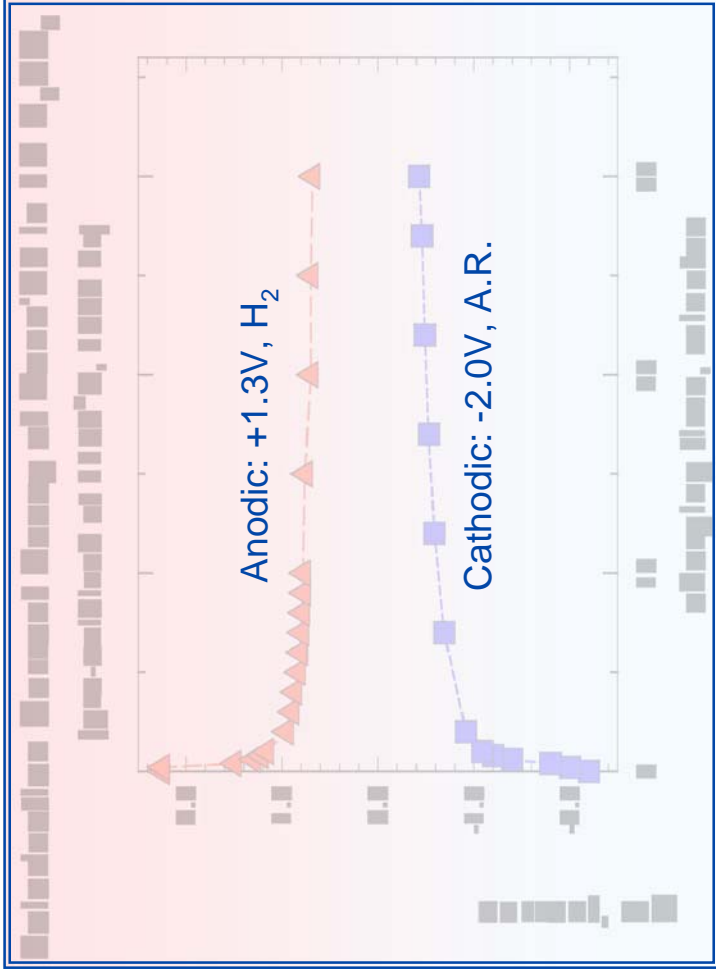
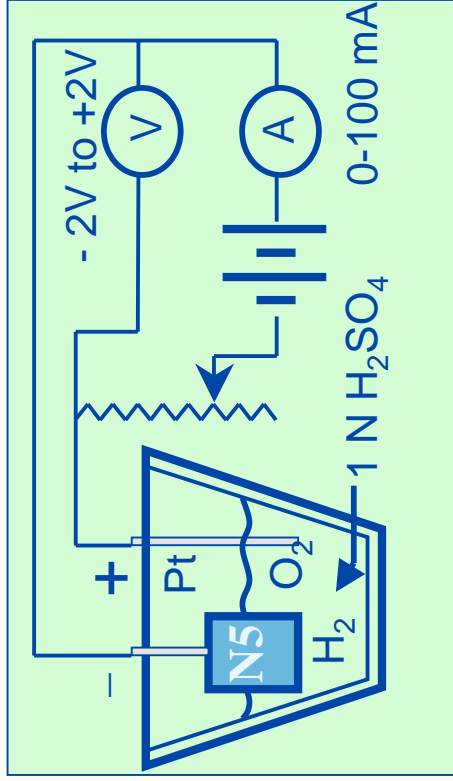
Occam's Razor: keep it simple and draw from known experience



Critical experiment:

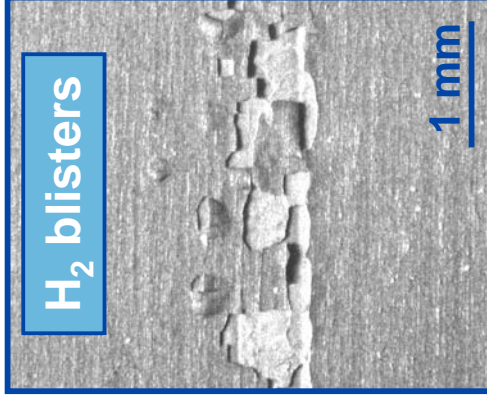
Test whether hydrogen charging causes scale delamination
(e.g., H-embrittlement of $\text{Ni}_3\text{Al}+\text{B}$, Kuruvilla, Stoloff, 1985)

Standard Electrochemical Cathodic Hydrogen Charging

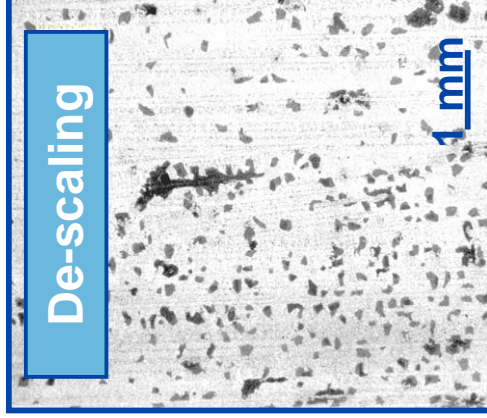




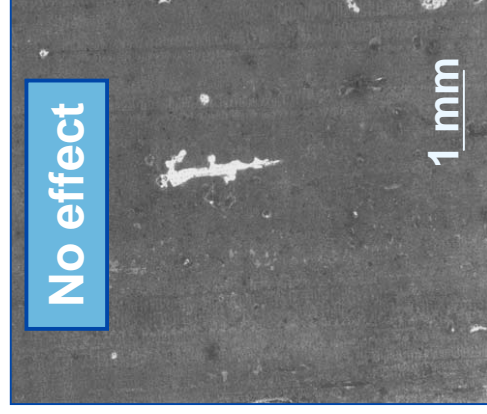
to -3.0 V

H₂ blisters

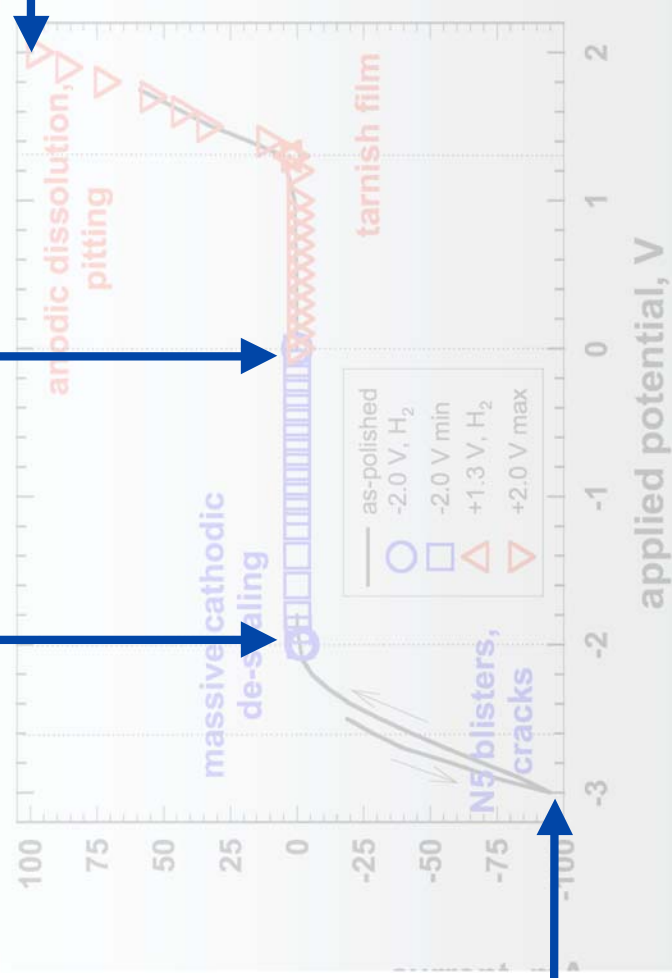
-2.0 V

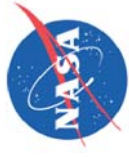
De-scaling

0.0 V

No effect

to +2.0 V

Dissolution



-2.0 V

Cathodic De-Scaling of Rene'N5
1 hr @ -2.0 V in 1N H₂SO₄

Exposed metal

Al₂O₃

250 GWBSE 7/7/2005

200um

Oxide imprints (SE)
in exposed metal

TaC

Al₂O₃

67-1 15.0kV 14.1mm x2.50k GWBSE 7/7/2005

20.0um

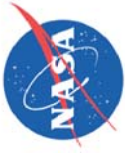
Pt

HfO₂

Al₂O₃

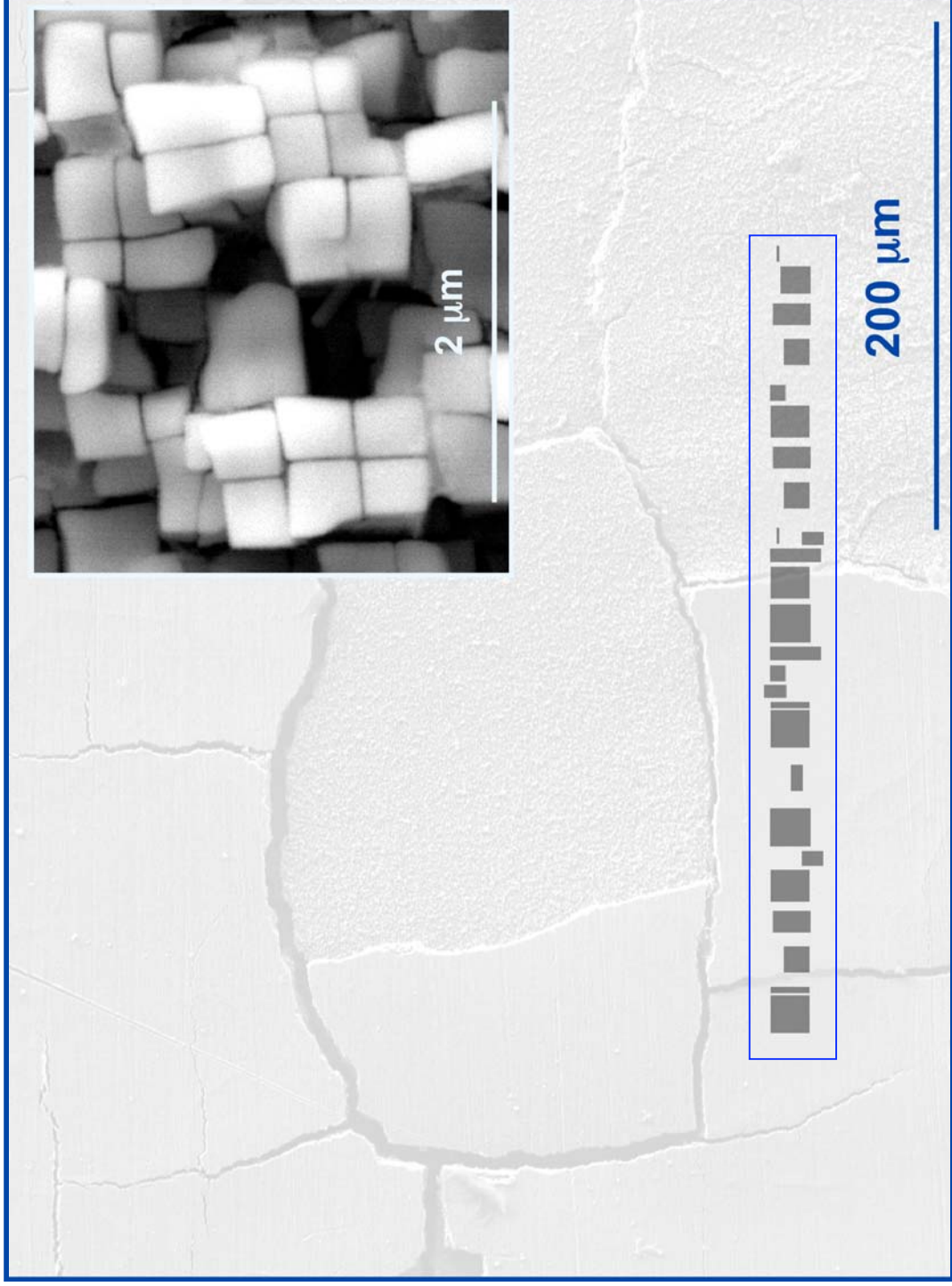
67-1 15.0kV 14.1mm x2.50k GWBSE 7/7/2005

20.0um



Cathodic Hydrogen Cracking and Blistering

γ' etching bare Rene'N5, -3.0V, 1 N H₂SO₄



H, S, (C?) synergistic weakening

Al₂O₃

YSZ TBC

Substrate

Spalled

Incubation

Intact

cathode

anode

e⁻

Al⁺⁺⁺(OH)₃⁻

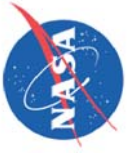
3H⁺

3H₂O

σ_{ΔCTE}

σ_{ΔCT}

τ_{spall3} << τ_{incubate2} << τ_{intact1}



Summary of MIDS Phenomenology (caveats)

- Intermediate sulfur content
- Mature, cycled (damaged) scales
(with exposed interface to humid environment)
- Water immersion as accelerated test
- Increases spallation, but may not be *necessary*
- H-charging failed adherent, but mature scales
- (Stabilization for intermediate P_{H_2O} aging?)

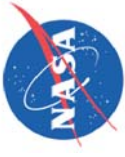


Connections and Proposed Hypothesis

1. **Primary** scale (TBC) chemical effect due to sulfur.
2. **Secondary**, delayed Al_2O_3 scale (and TBC) spallation
= **moisture** effects (MIDS, DTS).

Cathodic **H-charging** causes massive interfacial Al_2O_3 scale spallation at very low current (1mA at -2V).

: Interfacial hydrogen embrittlement is responsible for moisture-induced delayed failure of Al_2O_3 scales and thus contributes to Desk Top Spallation of TBC's.

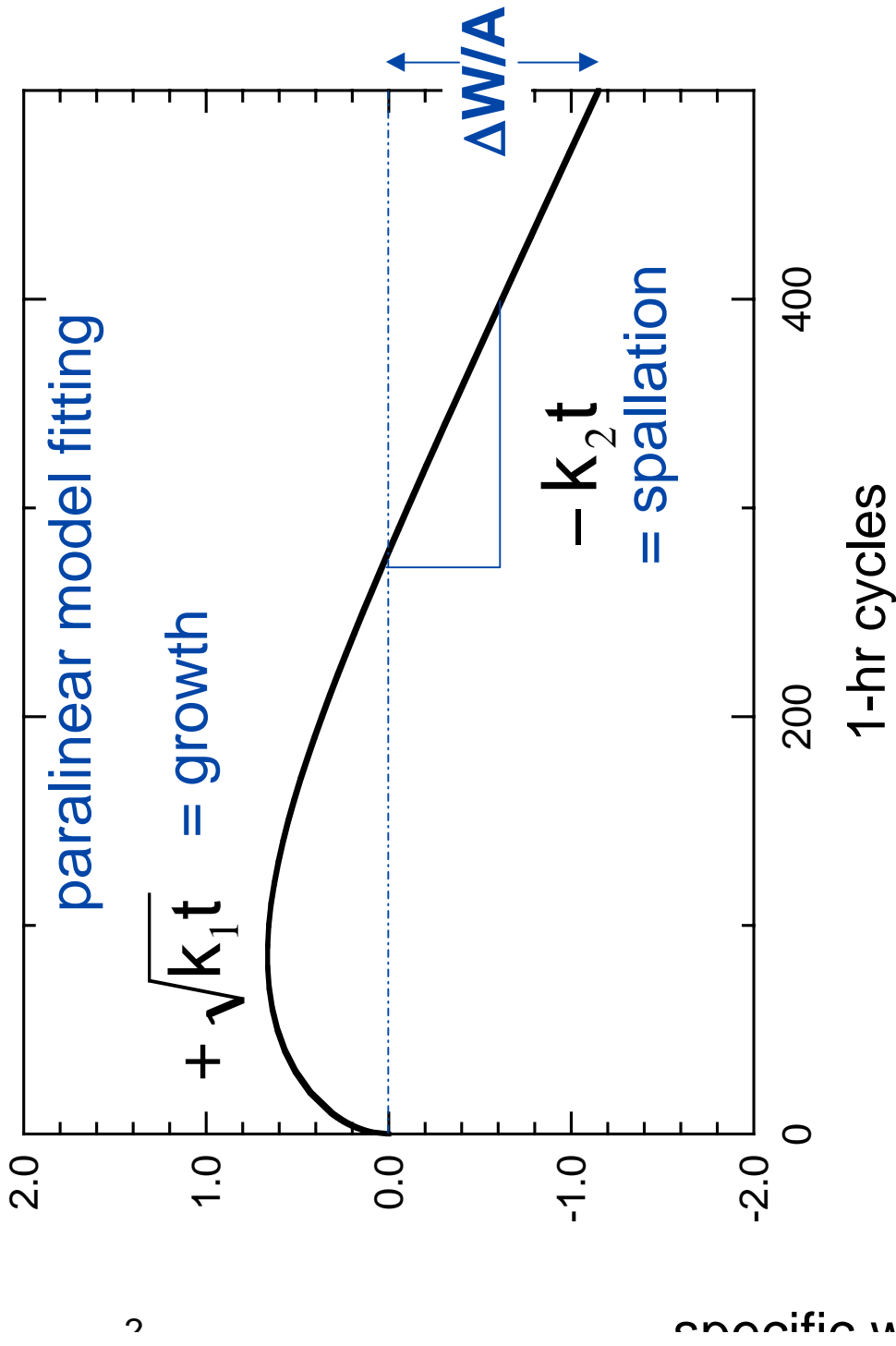


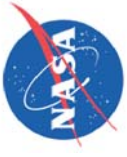
- **PWA 1484, Rene'142, Rene 'N5**
 - ***Critical Y/S ratio ~ 1:1 atomic (3:1 by weight)***
 - H₂-anneal improves adhesion (cyclic + immersion)
 - Evidence that ***moisture-assisted spallation***, is a ***hydrogen embrittlement*** phenomenon



Cyclic Oxidation Modeling:

$$\Delta W / A = f(\sqrt{k_1 t}, k_2 t)$$





Cyclic Oxidation Modeling

Basic Features

- **Postulate an oxide:**
(Al_2O_3 , NiO ,...); S_c = mass oxide/oxygen
- **Define the kinetic growth behavior:**
(parabolic k_p , power law k , m ...)
- **Define the spalling algorithm:**
(% spall = $Q_o \cdot \text{existing scale}$) $^\alpha$
(outer layer vs bare metal segments)
- **Perform iterative calculations; bookkeeping**
oxygen gain, oxide lost, metal consumed,...



Cyclic Oxidation Modeling

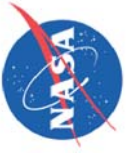
Common Variations (COSP)

GROWTH	parabolic	$\left(\Delta W / A\right)^2 = k_p t$
	power law	$\left(\Delta W / A\right)^m = k_p t$
	logarithmic	$\left(\Delta W / A\right) = \ln \{(kt + c)\}^{1/m}$
	SPALL FRACTION	
SPALLATION	uniform thickness	$F_S = Q_o W_r'^{\alpha}; \alpha = 1$
	Monte Carlo (bimodal)	$F_S = Q_o W_r'^{\alpha}; \alpha = 1$
		$R_{\text{spall}} = \frac{\text{spall depth}}{\text{total scale thickness}}$
	DICOSM	$F_A = \text{spall area fraction (thickest segment)}$
	p - k _p ; (Monceau)	p = spall (area) probability

A) cycle number, **(j)**, less than number of area segments, **(n₀)**

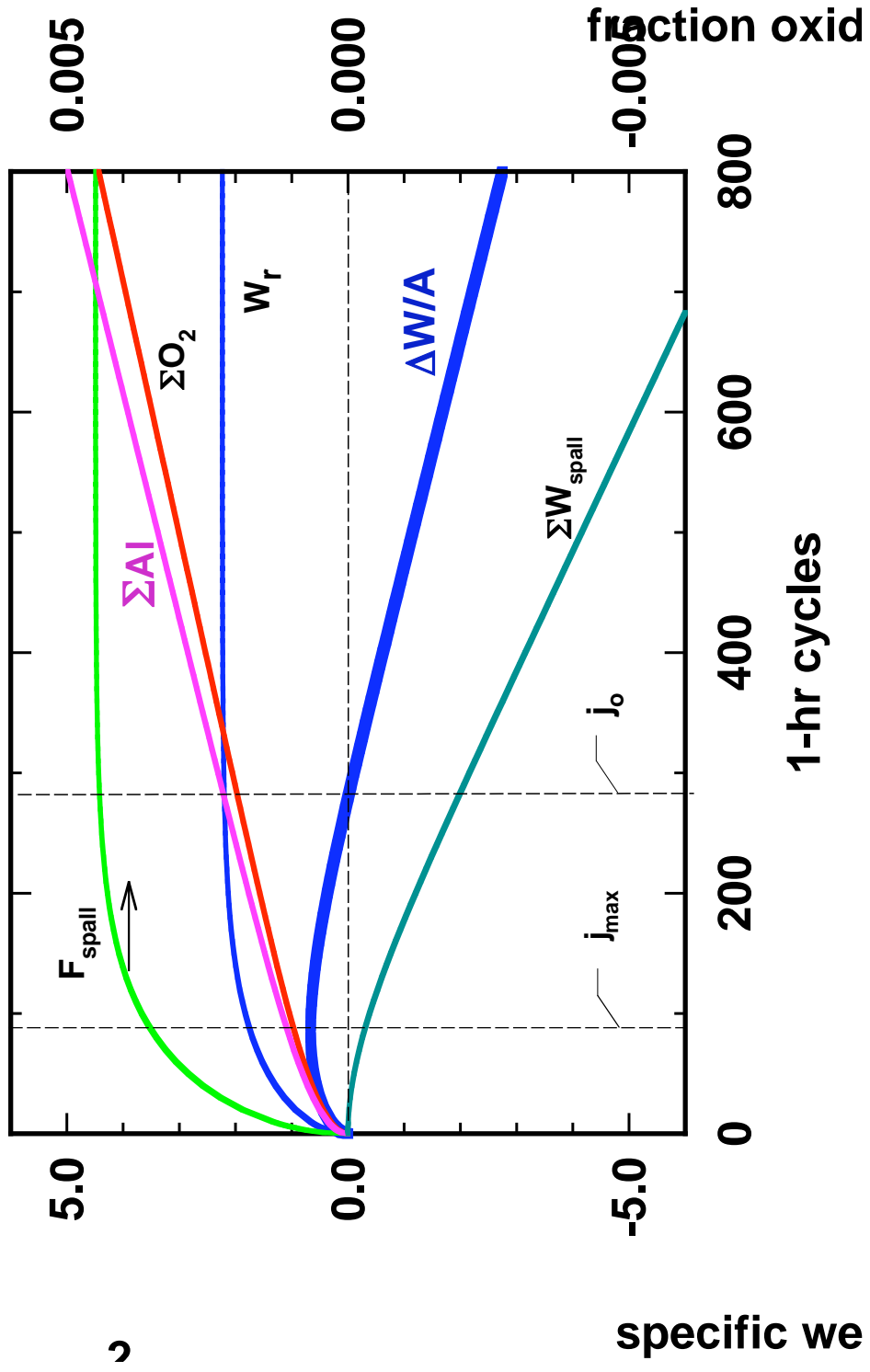






COSP Model Outputs

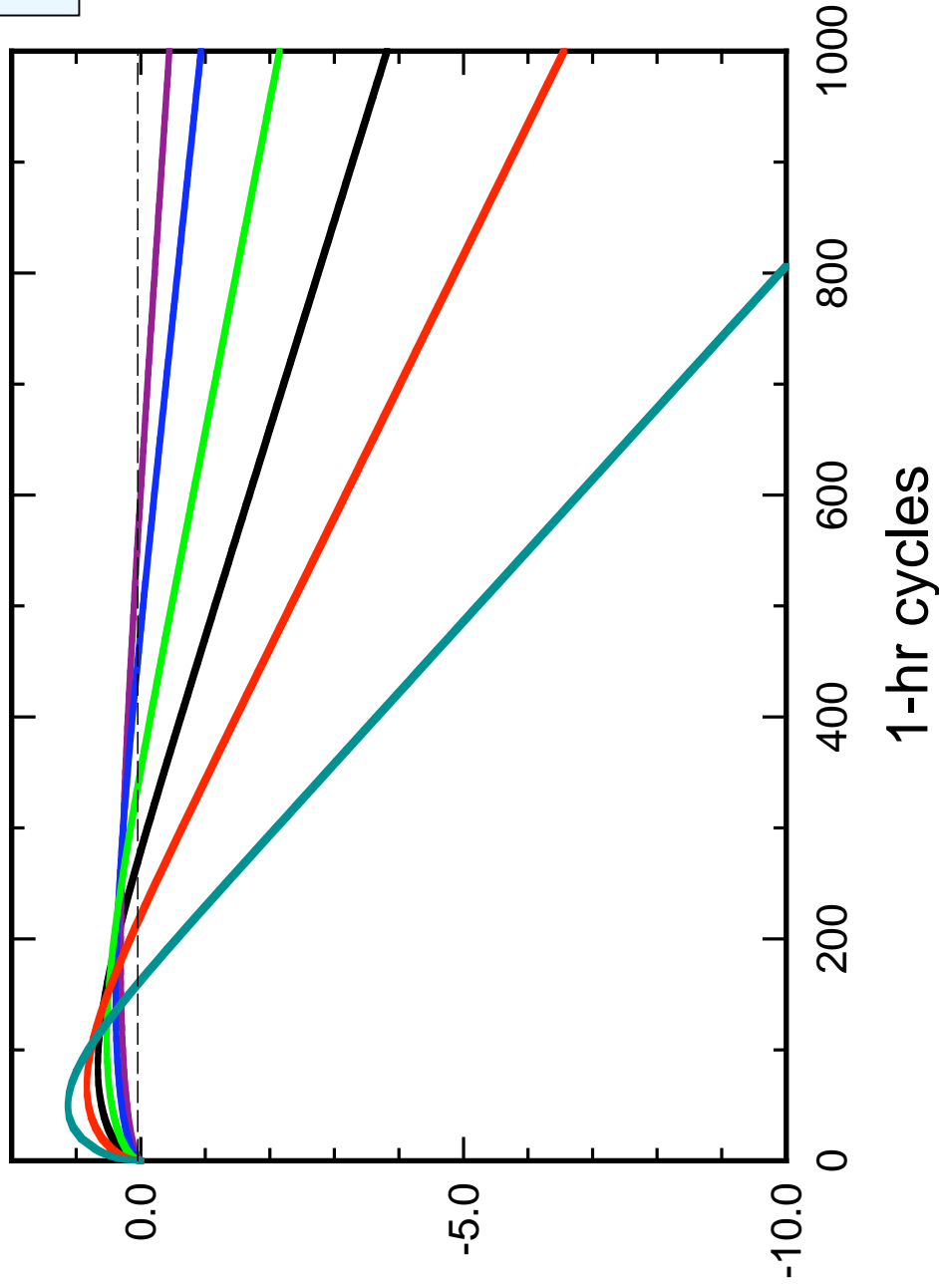
Al_2O_3 scale, $k_p = 0.01 \text{ mg/cm}^2$, $\Delta t = 1 \text{ hr}$,
 $Q_o = 0.002 \text{ cm}^2/\text{mg}$, $\alpha = 1.0$





Parametric Study: Effect of k_p

(parabolic, Al_2O_3 , $Q_o=0.002$, $\Delta t=1$ hr)



k_p
(mg^2/cm^4hr)

0.001

0.002

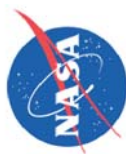
0.005

0.010

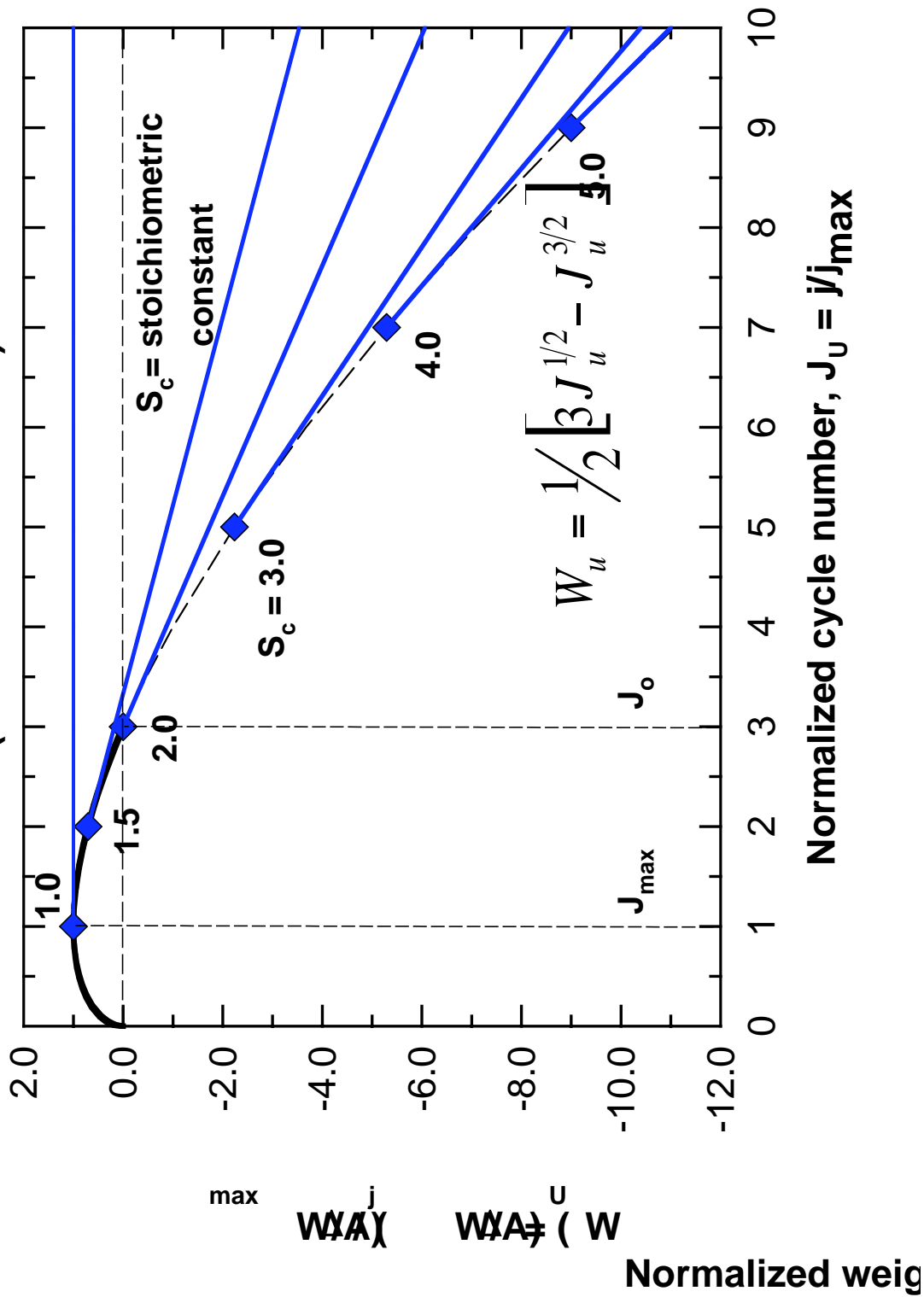
0.020

0.050

specific

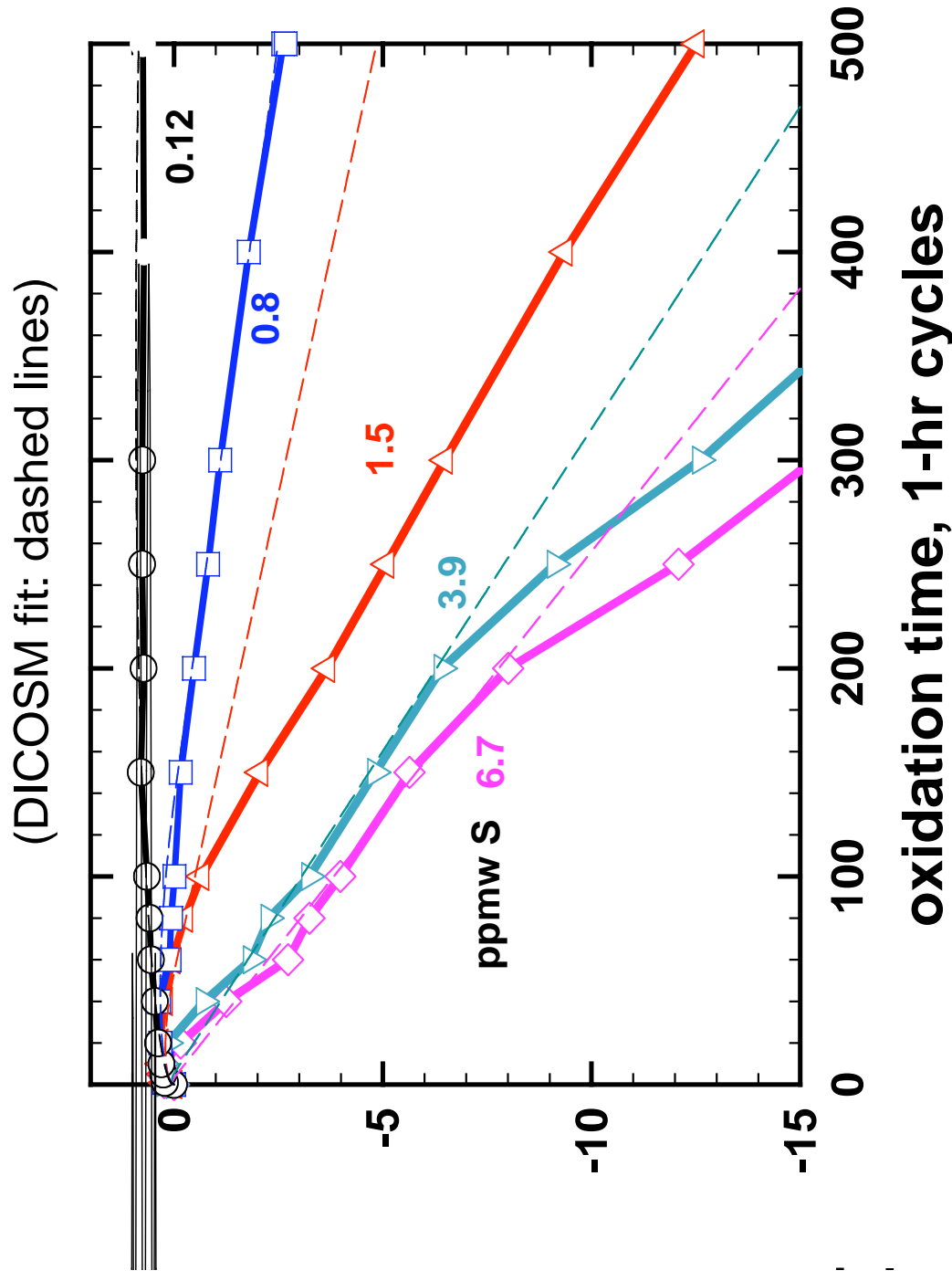


Semi-universal Cyclic Oxidation Curve (DICOSM-GSA model)



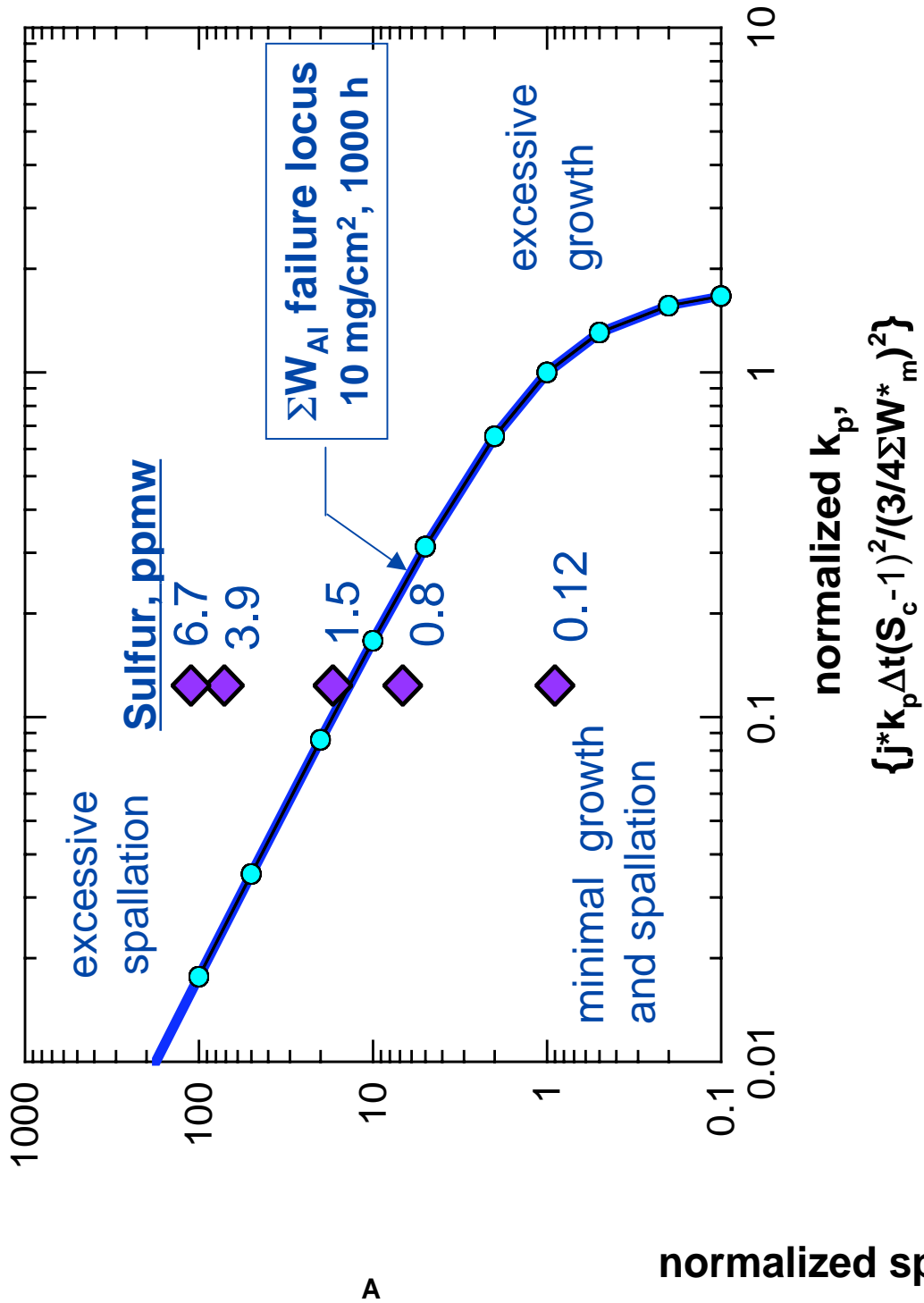


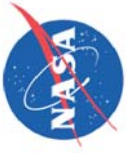
Effect of Sulfur Content on the 1100°C Cyclic Oxidation of PWA 1480





Universal Cyclic Oxidation Life Map PWA 1480, 1100°C





- **Cyclic Models**
 - User – friendly COSP for Windows (multiple models, instant plots, uploads expt'l data)
 - Produce typical plots; fits ideal alloy behavior
 - DICOSM, $p-k_p$ allow analytical solutions, trends, universal failure maps.



Final Recap

1. About 0.2 ppmw S (or Y/S ratio of 1:1) is critical.
2. Interfacial hydrogen embrittlement causes moisture-induced delayed failure (MIDS) of Al_2O_3 scales.
3. Ideal cyclic behavior can be analyzed by models.



- J.L. Smialek: "Oxidation Resistance and Critical Sulfur Content of Single Crystal Superalloys," Transactions of the ASME, Vol. 120, 1998, pp. 370-374.
- J.L. Smialek: "Toward Optimum Scale and TBC Adhesion on Single Crystal Superalloys," High Temperature Corrosion and Materials Chemistry, E.J. Opila, P.Y. Hou, D. Shores, M. McNallan, and R. Oltra, eds., The Electrochemical Society Proceedings, volume 98-9, Pennington, NJ, 1998, pp. 211-220.
- J.L. Smialek, J.A. Nesbitt, C.A. Barrett, and C.E. Lowell: "Cyclic Oxidation Testing and Modeling: a NASA Lewis Perspective," in the European Federation of Corrosion, *Cyclic Oxidation of High Temperature Materials*, Institute of Materials, London, (1999), M. Schutze and W.J. Quadakkers, pp. 148-168. (Also NASA TM 2000-209769).
- J.L. Smialek: "Maintaining Adhesion of Protective Al₂O₃ Scales," *JOM*, January 2000, pp. 22-26.
- J.L. Smialek: "Advances in the oxidation resistance of high-temperature turbine materials," *Surface and Interface Analysis*, **31**, 582-592, 2001.
- J. L. Smialek and B. A. Pint, "Optimizing Scale Adhesion for Single Crystal Superalloys," *Mater. Sci. Forum*, **369-372**, 459-66 (2001). (also NASA TM 2000-210362).
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